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REPORT OF THE PESTICIDES TECHNICAL COMITTEE TO THE LAKE MICHIGAN ENFORCEMENT CONFERENCE ON SELECTED TRACE METALS

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THE PESTICIDES TECHNICAL COMMITTEE
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THE LAKE MICHIGAN ENFORCEMENT CONFERENCE
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16. Abstracts Report is concerned with the existing knowledge of selected trace metals in the water, sediments, and aquatic life resources of Lake Michigan and its tributaries. Information is presented on the sources of these metals i. e., industries, municipal sewage treatment plants, and atmospheric fallout. Metals reported on include cadmium, chromiu, lead, nickel, zinc and others. While data are available on water concentrations of heavy metals in Lake Michigan and its tributaries, levels of sensitivity and number and frequency of samples are inadequate to establish present conditions. Airborne emissions from power plants, steel mills and incinerators may be contributing significant amounts of some metals to the lake environment. Heavy metals usually are found in sediments at much higher concentrations than in the overlying water, but information is lacking as to the ecological significance of these accumulations in varied environments. Estimates of probable safe ranges for Lake Michigan fish are given for copper, nickel, zinc, cadmium, and chromium. Committee made general recommendations about future monitoring efforts, analytical methodology, and research needs. Bibliography.

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INTRODUCTION

The Lake Michigan Interstate Pesticide Committee was created in 1968 to advise the Enforcement Conference in the matter of pesticide contamination of Lake Michigan and its tributaries. Based upon subsequent charges, the committee's work included study of contaminants other than pesticides. Presently the committee functions more as a toxic substances advisory body. In this functional capacity, it has considered the potential problems of PCB's, pthalates, and selected trace metals which may be of biological significance.

Although mercury caught the scientific community offguard, the potential problems associated with other metals - zinc, copper, chromium, etc. - are not new. Scientists have been studying the effects of these metals on the aquatic ecosystem for many years. While some of the committee members have been deeply involved in such studies, as they related to parochial jurisdiction, it became increasingly clear that no one was looking at the big picture: What is the general situation on metals in Lake Michigan? With this question in mind, the committee asked each state member in 1971 to submit selected trace metal data for Lake Michigan and its tributaries. This report represents a compilation of the data submitted and hopefully will answer the question posed previously. Basically, the report is concerned with the existing knowledge of selected trace metals in the water, sediments, and aquatic life resources of Lake Michigan and its tributaries. Some information is also presented on the sources of these metals i.e., industries, municipal sewage treatment plants, and atmospheric fallout. More information is needed.

The material presented herein represents a sincere and conscientious effort to put together the available literature on selected trace metals. No attempt was made to do an exhaustive search of the literature. However, the committee believes that this report is sufficiently representative of existing knowledge that it warrants the conclusions and recommendations drawn.

Persons knowing of past, present, or on-going studies which fall within the scope of this report, but which are not included, are requested to send copies to the committee chairman.

SUMMARY

An attempt was made to pull together available literature and unpublished data to see what is known about selected trace metals in the Lake Michigan Basin. The metals selected are those which may, even at very low concentrations, cause problems to aquatic life or humans.

Although data are available from many different sources, no attempt is presently being made to monitor the overall conditions within the Lake Michigan Basin. Little is known about the sources and amounts of metals now entering the Lake. Airborne emissions from power plants, steel mills, and incinerators may be contributing significant amounts of some metals to the Lake environment. More study should be encouraged so that reliable estimates can be made and the true significance of airborne emissions established.

While data are available on water concentrations of heavy metals in Lake Michigan and its tributaries, the levels of sensitivity and number and frequency of samples are inadequate to establish present conditions. Zinc occurs in high enough concentrations so that it is detectable using present techniques. Copper, cadmium, nickel, lead and chromium, are generally below detectability in Lake Michigan. Heavy metals in both Indiana and Michigan tributaries are often below the level of detectability, and little information is available from Wisconsin tributaries. Recent data indicate that the Grand River may be a significant source of copper, nickel, chromium, and zinc to the southern basin of the Lake. The Environmental Research Group, Inc. recently sampled Lake Michigan waters, sediments, and aquatic organisms to establish a baseline for 35 elements. Some biologically important metals such as cadmium and nickel were not included, but their work may begin to provide a baseline for some metals in Lake Michigan.

Generally, however, analytical sensitivities for metals in water samples must be improved before any meaningful conclusions about the actual heavy metals concentration in Lake Michigan and the contribution of the tributaries to these levels can be established. Furthermore, tributaries must be sampled at various flow stages to enable an estimate of sources and mass balance to be made. It is imperative that sufficient data be obtained to determine if metals concentration in Lake Michigan is increasing in order to predict whether harmful levels are likely to be reached.

Heavy metals usually are found in sediments at much higher concentrations than in the overlying water, but information is lacking as to the ecological significance of these accumulations in varied environments. Metals in sediments are potentially available for

uptake by some organisms and may accumulate through the aquatic food chain. Since the information available does not permit us to reliably predict whether or not various metals will be reconcentrated in aquatic organisms from bottom sediments, such deposits must be viewed with concern.

The data indicate that mercury, lead, zinc, chromium, copper, and arsenic are accumulating in the uppermost (recently deposited) sediments (0-10 cm) of the deeper regions of southern Lake Michigan (see Table 6). Trace elements which show little or no accumulations in the top layers of sediment are boron, cobalt, beryllium, lanthanum, manganese, nickel, scandium, and vanadium. Significant areas of concentration of chromium, mercury, arsenic, copper, lead, and zinc occur off Grand Haven and Benton Harbor in Michigan, off of Waukegan in Illinois, and in the center of the Lake near the Illinois - Wisconsin border.

Studies by the Illinois Geological Survey show a good correlation with organic carbon distribution in sediments and concentrations of certain elements. These correlations suggest that elevated levels of certain metals in top sediments are the result of man's recent activities in the watershed surrounding Lake Michigan and perhaps are related to increased biological productivity.

Further studies of metals in sediments by the State of Michigan and the U.S. Geological Survey have clearly established that municipal and industrial discharges are important sources of metals.

Not enough is known about heavy metals in tributary sediments and their movement to calculate a poundage input of heavy metals to Lake Michigan from sediments. Since the significance of metals in sediments is unknown, monitoring of stream and lake sediments is necessary to locate contaminated areas and sources of heavy metals to the Lake Michigan ecosystem. The existing potential "hot spots" should be watched carefully for problems such as the one which developed over the methylation of mercury in sediments by bacteria. The sources of heavy metals should be controlled so further deposition is eliminated or decreased.

It appears that except for mercury, metal residues in fish do not exceed concentrations that are likely to be selected if Food and Drug Administration action levels were to be established. The data are insufficient in quantity, and sampling and analyses have been too variable to permit best use of existing data.

Data on the acute toxicity of metals using Lake Michigan water and fish are not available. However, it is possible to estimate the probable safe ranges using existing bioassay data to estimate the 96 hr. TLm values for Lake Michigan fish and water.

Estimates of probable safe ranges for Lake Michigan fish are given for copper, nickel, zinc, cadmium, and chromium. Estimates of probable safe concentrations for other metals must be based on 1/100 of the 96 hr. TLm until data are available upon which better predictions can be made.

RECOMMENDATIONS

1. There is an urgent need to establish acute toxicity levels (TLm) for selected metals using Lake Michigan water and various life stages of Lake Michigan fish. Such information will make it possible to establish recommended safe levels for selected metals in Lake Michigan. Until this information is available, we must use available bioassay data to establish probable safe ranges.

2. The states should report regularly on the inputs of metals to the Lake Michigan Basin, based on information obtained from industrial permit programs and tributary monitoring. Sewage treatment plant effluent should also be monitored to determine the input of metals from this source.

3. Analytical and field methods must be standardized for all heavy metals research programs to insure that data obtained is accurate and precise and contributes to a body of comparable data. The Interstate Pesticide Committee has taken a step toward resolving this problem by having a meeting on August 23-24, 1972 of the working chemists from agencies represented on the Committee.

4. An attempt should be made to determine the contribution of airborne emissions of metals to the waters of Lake Michigan and its tributaries.

5. While the Committee feels that the present levels of selected trace metals are not a problem at this time, the Food and Drug Administration guidance should be obtained to establish acceptable levels of these metals in fish.

6. The levels of selected trace metals in Lake Michigan waters and fish should be clearly established at this time. A program to monitor changes in these levels and to establish future trends is also needed.

7. An effort should be made to understand the ecological significance of metals in sediments. The potential impact of such compounds as NTA on the metal deposits in sediments should also be explored.

ACKNOWLEDGEMENTS

Someone had to do the work. Each state committee member searched his state's files for published and unpublished data. Ms. Ginny Snarski with the EPA National Water Quality Laboratory in Duluth, Minnesota took the mass of material and wrote the first draft. Dr. Donald Mount, Director of the Duluth Laboratory provided guidance and edited the draft. Mr. Chris Potos, Chief, Water Quality Standards, EPA, Chicago, and Mr. Gary Milburn, also Water Qualtiy Standards, Chicago, helped write the final draft with guidance from the committee. Mr. John Hesse, Michigan Water Resources Commission, will present the Summary and Recommendations from the Report at the reconvening of the Lake Michigan Enforcement Conference on September 19, 1972, in Chicago, Illinois.

Special thanks must be given to Ms. Janet Mason, Enforcement Division, EPA, Chicago, who redid many of the graphs and saw to it that the report was completed on time, and to Ms. Alice Barrera, Ms. Mary Ann Cameron, Ms. Bernie Hughes, and Ms. Carol Foglesong for typing and proofreading the final version.

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REPORT ON
SELECTED TRACE METALS
IN
THE LAKE MICHIGAN BASIN

SOURCES OF TRACE METALS

Natural levels of metals exist in the aquatic environment. These natural levels in the water are influenced by the geological formations in the watershed because metals leach out of rocks or erode from surrounding land. The chemical characteristics of both the minerals and the water affect the rate at which the metal enters the water. Man's activities also have a significant effect on their levels. Construction, agriculture, and mining increase erosion and leaching of metals from ores, and metals are widely used and discharged in industrial processes throughout the country. Table 1 gives consumption figures for metal usage in the United States and Table 2 lists common uses.

Little is known about sources of metals in the Lake Michigan basin and the amounts introduced into the Lake are presently unknown. Based on the types of industries found in the Lake Michigan basin, a list of tributaries with metals which might be present in more than "background" levels is given in Table 3. Information on quantities of metals discharged to the basin by industries could be obtained from State and Federal permit programs. As these programs improve and industrial effluent monitoring becomes a reality for all industries, it will be possible to establish the contribution from these sources and future trends. To date, little or no attempt has been made to compile this data for the Lake Michigan basin.

AIRBORNE SOURCES OF WATER POLLUTION

Winchester and Nifong (1971) suggest that certain trace elements which are strongly associated with air pollution sources in the Lake Michigan basin may be contributing significantly to lake water pollution by an atmospheric fallout route. A partial inventory of air pollution emissions for 30 trace elements was presented for the Chicago, Milwaukee, and northwest Indiana metropolitan areas, based on available published information (Table 4).

The major sources of air pollution which contribute trace elements to the atmosphere over southern Lake Michigan are:

(1) Coal burned for electrical and heating uses.
(2) Emissions from coke ovens in the manufacture of metallurgical coke.
(3) Fuel oil burned for electrical and heating needs.
(4) Automotive fuel burned for transportation.
(5) Emissions from iron and steel manufacturing facilities.
(6) Emissions from cement manufacturing plants.

The inventory is then compared with actual stream inputs measured by the Federal Water Pollution Control Administration (1968) for Zn, Cu, and Ni. A calculated total inflow rate based on the composition of each stream and its gaged annual flow are given (Table 5). Evidence indicates that the atmosphere may now be a major source of Zn in Lake Michigan, and atmospheric inputs of Cu and Ni may also be considerable. Moreover, the evidence suggests that air pollution probably exceeds expected unpolluted stream inputs for many additional elements in Lake Michigan.

A calculation is also presented of the time required to raise the Lake concentration by an ecologically significant increment (0.1 $\mu g l^{-1}$) through fallout (Table 6). Values ranged from 0.06 years for iron to 500 years for cadmium.

In spite of the extremely fragmentary nature of available data on air and water composition and on meteorological factors, air pollution appears to be an important water pollution source for certain elements. More importantly, this study highlights the need for more comprehensive information in order to formulate exact chemical models for inputs and outputs of contaminants to Lake Michigan.

Robinson and Landstrom (1971) sampled tributaries to Lake Michigan for trace metals, calculated poundage inputs, and compared these to atmospheric contributions calculated by Winchester and Nifong. The work by Robinson and Landstrom is further discussed under the section Heavy Metals in Water - Tributaries. They concluded that the atmospheric route is a significant potential source of Fe, Mn, Cu, Ni, and Zn to waters of Lake Michigan and its tributaries.

TRACE METALS IN WATER

INSHORE AND DEEPWATER AREAS

Deepwater (defined as that portion of the lake greater than 10 miles from shore) studies of heavy metal levels were conducted from May 1962 to November 1963 as part of a comprehensive study of Lake Michigan by the Great Lakes - Illinois River Basins Project (FWPCA, 1968). Because it constitutes the bulk of the lake waters and because it is least influenced by pollution, the deepwater area was chosen as a base line of water quality. Copper, chromium, nickel, and zinc were found to occur in the range of 5 to 20 ppb as shown in Table 7. Cadmium was not detected in the open waters. The levels of sensitivity were 10 ppb for rivers and wastes and 5 ppb for lakes.

Major inshore areas and tributaries were also a part of this study and trace metals were found in appreciable concentrations in them. Copper concentrations were usually the highest (70 to 140 ppb), followed by nickel (10 to 40 ppb) and zinc (20 to 110 ppb). Nickel concentrations in the Sheboygan River were three times higher than in the other rivers studied: Manistique, Manitowoc, Milwaukee, Burns Ditch, St. Joseph, Kalamazoo, Grand, Muskegon, and Pere Marquette Rivers. Cadmium concentrations in the St. Joseph River averaged 20 ppb and chromium levels found in the Grand River ran 40 ppb.

Heavy metal analyses were made from samples from Traverse Bay, Indiana, Chicago, and Milwaukee Harbors. Copper and cadmium was less than 5 ppb in these four locations and zinc was detected in Indiana Harbor (9 to 87 ppb) and in Calumet Harbor (25 to 53 ppb). Chromium (5 ppb) and nickel (5 to 9 ppb) were detected in Milwaukee Harbor samples.

Further studies were made of Lake Michigan waters in 1970. One hundred-eighty Lake Michigan water samples were collected by the Lake Michigan Basin Office, EPA (formerly FWQA) from August to October 1970, and were analyzed, unfiltered, by atomic absorption spectroscopy for copper, cadmium, nickel, zinc, lead, and chromium; 98 samples were analyzed for mercury. Since most of the samples were below the levels of detection for copper, cadmium, nickel, lead, chromium, and mercury, nothing conclusive can be said about these heavy metals in Lake Michigan except that they are <5 ppb. Since zinc was above detectability in all of the samples, a fair idea of the zinc concentrations in Lake Michigan can be gained. Most of the samples contained zinc from 5 to 50 ppb, but there appears to be no difference in zinc concentrations related to depth (See Figure 1). Zinc concentrations appear to be similar among inshore areas near Green Bay, and in southern and northeastern Lake Michigan; and the distribution of concentrations in inshore samples was the same as that in open lake samples (Figures 2-4). Little can be deduced from the histograms for other metals.

Recently, Copeland and Ayers (1972) and the staff of Environmental Research Group, Inc. in Ann Arbor, Michigan completed a comprehensive survey of trace metals in water, sediment, phytoplankton, zooplankton and benthos of Lake Michigan. One of the purposes of the survey was to determine the stable isotope make-up of Lake Michigan and its component sediment and biota. The survey also attempted to determine any biological changes presently occurring and to what extent the chemical and biological make-up of Lake Michigan has been altered by man.

Samples for the survey were collected by the Great Lakes Research Division of the University of Michigan from sites indicated on the map in Figure 5. Sampling was conducted during three cruises in the period August 1969 to June 1970. Water samples, taken at depths of less than one meter, were Millipore filtered in an all glass apparatus and then acidified with 1 ml of nitric acid. The filters were placed in plastic bags and frozen. Each sample was analyzed for 35 trace elements using neutron activation and atomic absorption. The 35 trace elements include antimony, arsenic, chromium, cobalt, copper, gold, iron, manganese, mercury, molybdenum, selenium, silver, vanadium, and zinc (Table 8). No analysis was done for beryllium, cadmium, lead, or nickel.

Table 8 lists the average concentrations of all elements measured in water, sediment, biological samples for Lake Michigan. It was concluded, in part, that Lake Michigan and its components are quite typical of the world as a whole and on the average exhibit no unusual or unexpected results.

However, in analyzing the distribution of trace elements in water samples, it was concluded that chromium and zinc showed sufficient geographic distribution over the lake to suggest a major source. The Grand River was suggested as the source of these high concentrations. Further data from this report is presented in the sections on Sediments and Accumulations of Heavy Metals by Aquatic Organisms.

Illinois

Fifty-one water samples collected from water plants and from open water by the Illinois Environmental Protection Agency were analyzed for copper, cadmium, lead, zinc, hexavalent chromium, trivalent chromium, arsenic, barium, and manganese. One hundred-eighty samples were analyzed for iron and 43 for mercury; 12 were from water treatment plants and 31 from the open lake taken in August and October 1970. No mercury was detected in any of the samples at the lowest level of detectability, 1 ppb. Analyses for heavy metals showed measurable readings only for zinc and iron.

Michigan

In 1967, Michigan sampled 11 interstate water intakes in the Lake Michigan basin and analyzed them for copper, zinc, chromium and arsenic. All analyses were done colorimetrically with sensitivities of 10 ppb for chromium, 20 ppb for arsenic, and 100 ppb for copper and zinc. No

concentrations exceeding the limits of detectability for these metals were found. The water intakes checked were: St. Joseph, Benton Harbor, South Haven, Holland, Grand Rapids, Muskegon, Ludington, Northport Point, Traverse City, Escanaba, and Menominee.

TRIBUTARIES

Because few data exist on the present concentrations of most of the heavy metals in Lake Michigan, no comparisons can be made between levels in the tributaries and those in Lake Michigan.

In 1971, John A. Robbins and Edward Landstrom of the Great Lakes Research Division, University of Michigan made seven tributary sampling field trips and analyzed for 13 major and minor dissolved metals. Ca, Mg, Na, K, Fe, Mn, Cu, Ni, Cr, Mo, Zn, Sr, and Ba. Data presented is from one complete trip around Lake Michigan (Figure 6) in February of 1971 (Table 9) and four trips along the eastern side of the lake in May (two trips - Table 10-11), July (Table 12) and September (Table 13) of 1971.Table 14 shows the mean concentration and coefficient of variation for the five trips combined. Analysis of samples from the remaining two trips in June (complete trip) and October (eastern side) had not yet been completed when the report was written.

Surface water grab samples taken near river mouths, typically from bridges at mid-stream sites, were acquired by all-plastic collectors, immediately filtered through 0.45μ filters using a portable non-metal 2-liter capacity filter unit pressurized to 20 psig, with high-purity, dry nitrogen. Filtered portions, acidified for storage, were subsequently freeze dried in the laboratory and analyzed by means of atomic absorption spectrophotometry.

Persistent patterns were seen in the chemical composition of various tributaries. The Grand River was high in concentrations of Cu, Ni, Cr, and Zn as well as many major dissolved metals and is singularly high as a source of Cu, Ni, and Cr discharged into the southern basin of the Lake. Other persistent trends are high levels of Sr in the Manistee and Mo in the Pigeon. Correlations between some element concentrations can be understood in terms of geochemical associations.

Estimates of dissolved element inputs per day were made by using stream gauge data corresponding to the sampling dates. An example of the data used to make the calculations for chromium is shown in Table 15. Flow rates were corrected to include parts of a basin not gauged by up-stream stations by assuming the flow rate per unit drainage basin area to be constant. Mean daily loadings for the trace metals sampled were also calculated based on mean annual river flow rates (Table 16). Because of the Grand River's high flow rate and comparatively large concentrations, it is the largest source of 10 of the 13 trace metals determined. This River appears to be a singularly high source of Cr, exceeding its nearest

competitor, the St. Joseph - Paw Paw, by more than an order of magnitude, although it should be kept in mind that Cr levels fluctuate to an unusually high degree in the Grand River samples. The St. Joseph is usually the next highest source, except for loadings of Sr from the Manistee.

Mean daily tributary inputs of major and minor ions were calculated and compared (Table17) with inputs to the atmosphere from air pollution sources in the Chicago-Gary and Milwaukee urban industrial regions (Winchester and Nifong, 1969). It was suggested that the atmospheric route is a significant potential source of Fe, Mn, Cu, Ni, and Zn. The authors calculated that at least 20% of the daily emissions estimated in Table 17 would enter the lake.

They concluded that while several tentative conclusions could be drawn from their work, an extensive program of routine tributary monitoring combined with accurate, sensitive, chemical analysis is necessary to answer questions concerning detailed trends and representativeness.

In addition, while air pollution inputs of Zn, Cu, and perhaps other elements may be significant, especially locally in the southern basin of the Lake, refined estimates must await careful evaluation of atmospheric pollution levels over the lake and studies of particle transfer efficiencies to water surfaces.

Indiana

Heavy metal analyses were conducted by the Indiana State Board of Health on the Indiana tributaries to Lake Michigan from 1969 to 1971. Histograms are shown in Figures 7-10 for Indiana Harbor Canal and Trail Creek. Zinc levels in those two tributaries were higher than those found in Lake Michigan samples. About 70% of the samples were in the range of 50 to 250 ppb compared to a range of 5 to 50 ppb for most samples from Lake Michigan. Copper and nickel concentrations were about 10-fold higher also. Indiana's analyses included arsenic, but it was found only once at the level of detectability, 10 ppb.

Michigan

Since 1969 the Michigan Water Resources Commission has regularly conducted a Great Lakes Tributary Monitoring Program of water on a monthly basis at the mouths of 19 rivers tributary to Lake Michigan. A wide spectrum of chemical parameters have been measured at these sampling stations, but metals have not been included in all monthly analyses. During 1969 and 1970, the numbers of metal determinations on these were: Cu-160, Zn-164, Ni-145, Cd-119, Cr^{+6}-167, Cr^{+3}-11, and Pb-44. Analyses in 1969-70 were conducted on non-filtered samples, thus representing both the suspended and dissolved fractions. The lower limit of detectability for copper, zinc, nickel, chromium, and lead was 10 ppb and 1 ppb for cadmium. Of the 160 determinations for copper, 41.3 percent were above the limit of detectability; the mean of positive values was 19.8 ppb. The highest concentration detected was 300 ppb in a sample from the Menominee River. Seventy percent of the samples analyzed for zinc exceeded the 10 ppb

limit of detectability. Measurable values averaged 23.1 ppb with a high value of 480 ppb in a sample from the Grand River below Grand Haven. Cadmium was detected in only 1 of 119 samples. Hexavalent chromium was found in measurable concentrations in 11.2 percent of the samples. The positive values averaged 69 ppb with a high of 150 ppb found in the Grand River. The FWPCA study described previously also found high levels of chromium in the Grand River. Very few analyses were made for trivalent chromium. Cr^{+3} was detectable in 1 of the 11 samples at the concentration of 30 ppb. Lead was detected above the 10 ppb limit of sensitivity in 2 of the 44 samples analyzed; 50 ppb was measured in the Grand and Manistee Rivers.

Lake Michigan tributaries were sampled again in June 1971 for heavy metals. Unlike previous years, these samples were acidified and filtered through 0.45 micron filters in the field, but the lower limit of detectability for Cu, Ni, Cr^{+6}, and Pb remained at 10 ppb. Cadmium sensitivity remained at 1 ppb. The sensitivity for Zn was increased to 1 ppb. Silver, mercury, arsenic, cyanide, iron and manganese were also determined in these samples with limits of detectability of 10, 0.1, 10, 10, 10, and 10 ppb, respectively. Results of filtered samples were lower for copper, nickel, chromium, and lead than previous data on unfiltered samples. Few values exceeded the limits of detectability, but with the increased sensitivity, zinc was detected in 11 of the 19 tributaries at an average concentration of 3.3 ppb. Silver, mercury, arsenic, and cyanide were not detected in any of the samples. Iron and manganese were found in the majority of the tributaries at average concentrations of 246 and 92 ppb, respectively. Histograms of these data have been drawn for some of the heavy metals from six sampling stations on five Lake Michigan tributaries. These histograms in Figures 11-16 show the distribution of concentrations found in those rivers. The Grand River appears to have the highest concentration of copper and nickel.

As part of the Michigan Water Resources Commission's Interstate Rivers Monitoring Program, numerous sites on the Menominee and St. Joseph Rivers basins were samples for metal concentrations in 1971. All samples were filtered and acidified prior to transport to the laboratory. Concentrations of dissolved metals within the Menominee River basin were low. Nickel, hexavalent chromium, silver, mercury, lead, arsenic, and cyanide were not found above the limits of detectability at any station. Copper was detected at 10 ppb at one site in the upstream portion of the basin but was not detectable further downstream. Zinc was found at all stations in the range of 10 to 35 ppb and averaged 18 ppb. Cadmium occurred at 3 of 14 locations at a concentration of 2 ppb. A maximum of 100 ppb of iron was detected. Similar concentrations of these metals were found in the St. Jospeh River basin. Zinc occurred less frequently above the 10 ppb limit of detectability than in the Menominee River but averaged 16 ppb at

those stations where measurable. Again, no measurable levels of nickel, silver, mercury, lead, arsenic, and cyanide were found. Cadmium was measurable at 9 of the 37 stations with a maximum of 5 ppb. A high of 800 ppb of iron was found.

USGS Reconnaissance of Minor Elements

In October 1970, the U.S. Geological Survey sampled four locations within the Lake Michigan basin. Sampling locations included the Kalamazoo River at Parchment, Lake Michigan near Agnew, the Red Cedar River at Lansing and the Grand River at Grandville. Handling of the samples was comparable to those taken by the Michigan Water Resources Commission in 1971 in that they were filtered through 0.45 micron filters and acidified prior to shipment to laboratory. Analyses were conducted for arsenic, cadmium, hexavalent chromium, cobalt, lead, zinc, and mercury with the following limits of detection: 10 ppb for arsenic and zinc; 1 ppb for cadmium, hexavalent chromium, cobalt, and lead; 0.1 ppb for dissolved mercury; and 0.5 ppb for total mercury. Maximum concentrations detected in these four samples were 20 ppb arsenic, 1 ppb cadmium, <1 ppb hexavalent chromium, <1 ppb cobalt, 7 ppb lead, 200 ppb zinc, 0.2 ppb dissolved mercury, and 0.7 ppb total mercury.

Wisconsin

From May to October 1970, the Wisconsin Department of Natural Resources surveyed water and bottom sediments for mercury from major drainage basins in the state, public water supplies, and municipal sewage treatment plants (Konrad, 1971). All public water supplies contained less than 0.2 ppb mercury (the level of detectability) in raw and finished waters. Sewage treatment plants which accept sewage containing mercury were found to have elevated mercury levels in the sludge and in several cases in the final effluent. Sludges from Kaukauna, Portage, Green Bay, Kimberly, Madison, and Appleton contained 3, 7, 5, 6, 16, 20, and 29 ppm, respectively. However, only Madison, Appleton, and Portage were found to discharge mercury - containing effluents (2.5, 1.0, and 2.0 ppb, respectively). The report states that the sources of mercury in the Madison area include chemical laboratories (university and private), hospitals, and battery-manufacturers, but relative amounts from each of these sources are presently unknown.

The only other data available on other heavy metals in Wisconsin streams tributary to Lake Michigan are from a few samples taken in 1969 from the Fox River at Green Bay, Wisconsin, and the Milwaukee River at Milwaukee. The results are given in Table 18.

DISCUSSION

It is quite evident that data on water concentrations of heavy metals in Lake Michigan and its tributary streams are inadquate, in quality and quantity, to provide even an useful notion of conditions. Zinc occurs in high enough concentrations so that it is more often detectable. Copper, cadmium, nickel, lead, and chromium are below detectability in most of the water samples collected in Lake Michigan. A glance at the histograms of heavy metals in both Indiana and Michigan's tributaries shows a large portion of the samples are below the level of detectability, and little information is available for the heavy metals in Wisconsin tributaries. It is apparent also that recent workers have been using techniques with greater sensitivity. Frequency of sampling has also increased but much more needs to be done.

There are no adequate arsenic measurements from tributaries. Michigan and Indiana analyzed for arsenic but the analytical sensitivity was not sufficient. Some workers believe that arsenic may methylate, therefore, measurements for it may be very important. The controversy over mercury levels in fish is well-known by everyone. Recent data from the National Water Quality Laboratory indicates that concentrations of methyl mercury in water in the low part per trillion range result in residues in fish muscle that exceed the FDA 0.5 ppm action level; therefore, few of the existing mercury measurements have had a sufficiently low detectable limit.

Analytical sensitivity for metals in water samples has improved greatly in recent years. It is obvious, however, that much analysis is still done at levels of sensitivity which are not adequate. The sampling and analytical techniques now employed vary widely and lead to data with wide variations in accuracy and precision. Because of the problems inherent in measuring metal concentrations in the ppb and ppt range, a well thought out program of analytical quality control is an absolute necessity if the data is to be comparable. Much of the data thus far presented cannot be compared. Hopefully by drawing attention to the problem it will be more readily solved.

TRACE METALS IN SEDIMENTS

Heavy metals usually are found in sediments at much higher concentrations than in the overlying water. Metals are a normal component of geologic formations and they leach, erode, and eventually become a part of the sediment of surface water. Particles of metal-bearing rocks are separated by freezing and thawing and further ground and leached through weathering and abrasion. Metals adsorbed onto particulate matter settle, often aided by natural organic flocculents. If dissolved, they may be taken up by bacteria and higher organisms and later be returned to the sediment as the dead organisms settle to the bottom and decompose.

Man's activities are often a major factor when sediments are found to contain abnormally high concentrations of metals. Various metals are used in many industrial, chemical, and manufacturing processes. Wastewater discharges contain metals either as soluble ions or as suspended particles and usually result in downstream sediments with high concentrations of metals. Information is lacking as to the ecological significance of these accumulations in varied environments.

Some of the metals in sediments move into the overlying water by physical, chemical, or biological means. Changes in chemical characteristics of water alter the form of heavy metals in aquatic environments. Decreases in pH such as those associated with organic decomposition can cause precipitated metal compounds to dissolve. Likewise, increases in pH, such as those associated with photo-synthetic activity of algae, may cause dissolved metals to precipitate. The effect of pH on copper in water has been studied. Figure 17 shows the effect on the form of copper with a change in pH. At lower pH, soluble forms of copper, such as Cu^{++}, $CuOH^{+}$, and $Cu(OH)_2^{++}$, are prevalent in rather high concentrations. As the pH increases, the concentration of soluble forms decrease and the insoluble forms of copper are present in greater concentrations. Most of these reactions are accelerated by increased temperatures as well as currents that shift the bottom sediments, exposing new particles to the overlying water, allowing more solution to take place.

Burrowing aquatic organisms mix sediments and bring previously buried metal-rich sediments in contact with the water and enhance the solution of metals. Metals in sediments are potentially available for uptake by some organisms and may accumulate through the aquatic food chain. Since the information available does not permit us to reliably predict whether or not various metals will be reconcentrated in aquatic organisms from bottom sediments, such deposits must be viewed with concern.

Illinois Geological Survey Data

The greatest composite of data available on concentrations of metals in sediments within the Lake Michigan basin is a series of reports by the Illinois Geological Survey (Shimp, et. al., 1970; Rush, et. al., 1970; Shimp, et. al., 1971; and Kennedy, et. al., 1971). These reports are based upon the chemical analysis of southern Lake Michigan core and grab samples. By analyzing the core samples by depth interval, a history of the input of metals to Lake Michigan can be studied. Some caution must be exercised in such analyses, however, because translocation may occur after deposition.

The data indicate that mercury, lead, zinc, chromium, copper, and arsenic are accumulating in the uppermost (recently deposited) sediments (0-10cm) of the deeper regions of southern Lake Michigan (see Table 19). Good correlation exists between metal concentration and organic carbon content of the sediment as well. Trace elements which show little or no accumulation in the top layers are boron, cobalt, beryllium, lanthanum, manganese, nickel, scandium, and vanadium. Significant areas of concentration of chromium, mercury, arsenic, copper, lead, and zinc occur off of Grand Haven and Benton Harbor in Michigan, off of Waukegan in Illinois, and in the center of the lake near the Illinois - Wisconsin border.

Analyses show an accumulation of mercury at the top of the core (0.1 - 0.4 ppm) with the concentration decreasing down to .03 to .06 ppm at a depth of 10 to 15 centimeters or lower.

Sandy areas in the extreme southern end of Lake Michigan generally contain low concentrations of trace elements, and little accumulation has been observed in sediments at the sediment water interface.

Large sediment loads of streams at major river mouths have accumulations of metals at greater depths than the sediments in deeper regions of the lake.

Studies by the Illinois Geological Survey show a good correlation with organic carbon distribution in sediments and concentrations of certain elements. These correlations suggest that elevated levels of certain metals in top sediments are the result of man's recent activities in the watershed surrounding Lake Michigan and perhaps are related to increased biological productivity.

Michigan

The Michigan Water Resources Commission has undertaken a monitoring program to determine whether concentrations of metals in sediment

samples collected below industrial and municipal outfalls represent a significant problem. Ten stations selected as representative of non-contaminated streams, were sampled by the Water Resources Commission during a cooperative metals survey with the U.S. Geological Survey (USGS) in October 1970, to establish normal background levels for this area. Table 20 shows the ten stations sampled and the metal concentrations found.

During the October 1970 sampling, three stream locations below major municipal and industrial complexes were sampled by USGS and analyzed for the same metals (see Table 21). Concentrations of mercury, lead, and zinc at all three locations exceeded the ranges of background levels, but arsenic, cadium, chromium, and cobalt were not higher than at the background stations.

During collection of sediment samples in April and May 1970, as part of a state-wide screening program for mercury, duplicate samples were obtained for subsequent checks on other heavy metals. Dow Chemical Company, Midland, Michigan analyzed these samples using neutron activation. In addition to mercury, samples were analyzed for arsenic, copper, zinc, gold, cadmium, chromium, and antimony. The 35 locations sampled within the Lake Michigan basin (Table 22) were sites primarily at the mouths of major rivers and below large municipal and industrial areas likely to have been subjected to the influence of waste discharges. Comparison of the results with concentrations found at the 10 background water quality stations (Table 20) shows that all As concentrations were outside the range of samples taken at the background stations, as were 97 percent of the Zn concentrations, 14 percent of Cd, 80 percent of Hg, and 94 percent of Cr samples. Analyses of other metals show mean concentrations of 3.24 ppm antimony, 186.6 ppm copper, and 82.2 ppb gold. Clearly, municipal and industrial discharges are important sources of metals.

In a comprehensive water quality survey of the Kalamazoo River watershed in 1971, the Michigan Water Resources Commission collected sediment samples from ten stream locations within the watershed during August, and analyzed these for the presence of Ni, Cu, Zn, Hg, Cd, As, Pb, and total Cr (Table 23). Sampling sites were selected at locations throughout the watershed in order to provide a longitudinal comparison of metals concentrations. Concentrations ranged from 3.0 to 30 ppm for Ni, <1 to 50 ppm for Cu, 27 to 165 ppm for Zn, <0.1 to 0.44 ppm for Pb, and <10 to 48 ppm for total Cr. The lowest concentrations for each of the metals were tested in the north and south branches above any major municipalities. A sharp increase in concentrations of Zn, Cd, and total Cr was noted at station 3, located downstream from Marshall, Michigan. The concentration of Cd at this location was the highest found at any of the 10 sites. The Battle Creek River sediments, Station B-1, contained the highest Cu and As concentrations of any of the sites and also somewhat elevated levels of Zn and Pb. Station 7, downstream from the Battle Creek WWTP discharge, showed marked increases in Ni and total Cr concentrations in the sediments

as compared to those at station 6 above the WWTP. The highest Zn and Pb concentrations detected were at station 14, the first station downstream from Kalamazoo. Ni, Cu, Cd, and total Cr were relatively high at this location also. Concentrations of all the metals in the sediments at station 24 at Saugatuck were comparable to the low concentrations observed in the north and south branches.

Wisconsin

As part of their survey for mercury in major drainage basins, water supplies, and sewage treatment plants in Wisconsin, The Wisconsin Department of Natural Resources analyzed sediments from tributaries of Lake Michigan. Konrad (1971) suggests that the mercury-containing effluent from the Portage sewage treatment plant resulted in elevated mercury levels in the Upper Fox River sediments below Portage (3.7, 4.8, and 6.8 ppm) (see Table 24). The report states: "In general, it can be concluded that all bottom sediments contain at least trace amounts of mercury. Background levels range from 0.05 to 0.35 ppm with an average of 0.15 ppm." This agrees well with the range and average (range 0.13 to 0.24 ppm, average 0.17 ppm) Michigan found in their established background stations.

High sediment concentrations were found below the Wyandotte Chemical Company at Port Edwards on the Wisconsin River and below several pulp and paper mills on the Wisconsin, Chippewa, Flambeau, Wolf, Menominee, and Fox Rivers. No analyses on sediments for other heavy metals were provided by Wisconsin.

Copeland and Ayers (1972) of the Environmental Research Group, Incorporated also surveyed sediments in Lake Michigan. Their studies were concentrated on that portion of the sediment >200μ in diameter (Table 24). Average values for iron from these samples was 21,000 ppm for Lake Michigan as a whole. Manganese concentrations in sediments were quite variable. Several investigators have reported manganese nodules and manganese incrustations from various locations in Lake Michigan. It was suggested that the areas with highest concentrations represent similar conditions.

DISCUSSION

Not enough is known about heavy metals in tributary sediments and their movements to calculate a poundage input of heavy metals to Lake Michigan from sediments. Since the significance of metals in sediments is unknown, monitoring of stream and lake sediments is necessary to locate contaminated areas and sources of the heavy metals to the Lake Michigan ecosystem.

The existing potential "hot spots" should be watched carefully for problems such as the one which developed over the methylation of mercury in sediments by bacteria, and the sources of heavy metals should be controlled so further deposition is eliminated or greatly decreased. It is imperative that sufficient data be obtained to determine if metals concentration in Lake Michigan is increasing in order to predict whether harmful levels are likely to be reached.

ACCUMULATIONS OF TRACE METALS BY AQUATIC ORGANISMS

It is well-known that aquatic organisms concentrate heavy metals in their bodies to levels many times those in the water environment. Often although metal concentrations in the water are below the level of detectability, analyses of plankton and fish show substantial accumulations of these metals. Mercury in fish is a good example of this concentration phenomenon. Monitoring programs have shown many fish contain significant levels of mercury, often near the 0.5 ppm FDA "action level" while water samples are below detection levels of 1.0 ppb or less. Little is known about the relative contributions of water versus food-chain accumulation of mercury and other metals. It is most likely that in many cases both play a part. In a study on earthen ponds treated with sodium arsenite, Dupree (1960) found that plankton accumulated arsenic to several thousand parts per million after 30 days. He found small amounts of arsenic in the digestive tract of some bluegills, but little or no arsenic was detected in the flesh. However, in another study of ponds treated with sodium arsenite, Gilderhus (1966) found substantial residues of arsenic throughout the organs and flesh of bluegills.

Because fish have the capacity to accumulate trace metals either by direct water uptake or through food-chain accumulation, they can be used as indicators of levels in their environment. Different metals accumulate in different tissues in a fishes body. Mount (1964) in his development of an autopsy method for zinc found very high concentrations of zinc in the eye and kidney following 90-day exposure of bluegills to zinc. Skin and bone were the next highest, then gut and gills. Liver, muscle and spleen accumulated little, if any, zinc. Mount and Stephan (1967) found that cadimum accumulated in substantial concentrations in the kidney, liver, gill, and gut with lesser concentrations in the bone and muscle. Schiffman and Fromm (1959) found only small amounts of hexavalent chromium in fish muscle but significant amounts in the spleen, gall bladder, kidney, and liver. Schiffman (1961) found, however, that fish have little ability to store strontium in the body.

Because tissues have different affinities for metals, the value of whole body residue analyses is limited. In a fish important in the ecosystem as food for other fish, knowing the total body burden is helpful in assessing the potential danger to predator fish. From the human health standpoint, edible portion residues are the most useful, and FDA action levels are based on edible portions. A total body residue analysis would not yield the information necessary to determine whether the fish is "safe" for consumption or not.

Other aquatic organisms accumulate trace metals to rather high concentrations (see Table 25). Copper, iron, manganese and mercury concentrate to a larger extent in many types of organisms. Kidd (1970) suggests that the benthic amphipod, Pontoporeia affinis, distributed in most areas of Lake Michigan is a suitable monitor for manganese-54 and

zinc-65, but not for the isotopes of strontium. Lucas, et. al., (1970) reported the concentrations of trace elements found in fish from the Great Lakes. The range of concentrations in whole fish are listed in Table 25 also. Ranges of other elements observed in these Great Lakes Fish were 5 - 199 ppb antimony, 0.1 - 2.0 ppb selenium, and 1,100 - 4,800 ppb (1.1 - 4.8 ppm) zinc. Most of the cadmium, chromium, and copper was probably in the liver, kidney, and spleen and not in muscle.

Copeland and Ayers (1972) of the Environmental Research Group analyzed for some 35 elements in plankton and benthos of Lake Michigan (Table 8). Mercury was examined in detail in zooplankton, phytoplankton and benthos because of the recent findings of high concentrations of mercury in fish of Lake St. Clair and Lake Erie. It was concluded that there is no obvious pollution of mercury nor any obvious source of mercury in Lake Michigan. High concentrations and low concentrations tend to be near one another with no obvious trends. In general, however, the average values are higher in the central and northern parts of the lake as compared to the southern part. Since most of the stream input enters the lake in the central and northern portions and most of the population is centered in the south, it was suggested that mercury enters Lake Michigan as general stream input from a variety of sources, both agricultural and industrial. It was also concluded that the average concentration of mercury in Lake Michigan invertebrates is considerably below the levels found in fish in Lakes Erie and St. Clair and does not, at present, suggest excessive pollution.

Selenium, an element similar to arsenic in its toxicity, displayed an unusual geographical distribution in Lake Michigan zooplankton but not in phytoplankton or benthos. It was suggested that selenium concentrations were correlated with airborne fallout from the Chicago Metropolitan area. No other elements showed obvious geographical distributions in the biota.

Illinois

Edible portions of nine species of fish from Lake Michigan were analyzed by the Illinois Environmental Protection Agency for mercury, lead, and selenium content (see Table 26). Mercury levels averaged 0.303 ppm in 50 fish, lead averaged 0.165 ppm in 46 fish, and selenium averaged 0.311 ppm in 49 fish. All values are expressed on a wet weight basis.

Most species tested for mercury showed values near the average of 0.303 ppm. A composite sample of two carp from the Chicago area showed the lowest concentration of mercury found, 0.076 ppm. The highest concentrations of mercury, 0.654 ppm, was found in a composite of four goldfish from the North Chicago area. Although mercury values exceeded the interim FDA standard of 0.5 ppm only once, three coho salmon from the Chicago area had a value close to this action level.

In fish samples analyzed for lead, the coho salmon showed both the highest and the second lowest values. More variation occurred because there was a relatively high value found in a sample of four goldfish while samples of two carp and one carp X goldfish hybrid had low values.

Selenium concentrations in fish flesh showed a similar variation and average when compared to mercury. Values reported for selenium are considered somewhat higher than true values because it was not possible to obtain a true wet weight on samples that had been stored for a long period of time.

From this limited sampling, no trend was evident in either the predator or the bottom feeding fish and most values are within the expected ranges. The report concluded that further sampling is needed to obtain a clearer picture of the concentrations of heavy metals in Lake Michigan fish.

Michigan

The Michigan Water Resources Commission and the Fisheries Division of the Michigan Department of Natural Resources have conducted two cooperative surveys of heavy metals in fish in major watersheds draining to Lake Michigan.

Thirty-two fish samples collected in July 1970, from 18 stream locations (Figure 18) on the Grand River were analyzed for the presence of Cu, Ni, Zn, Cr, and Cd. Five of the samples were also analyzed for Hg. Concentrations of these metals ranged from <0.1 to 1.8 ppm 8.0 to 23.0 ppm Zn, <0.05 to 1.0 ppm Cr, and <0.01 to 0.45 ppm Hg. Ni was not detected above the limit of sensitivity of 0.4 ppm. Cd and Cr were detected only one and four times, respectively, above their limit of sensitivity of 0.05 ppm. (Table 27)

Fifty-two fish samples collected July 12-28, 1971, from 15 stream locations (Figure 19) on the Kalamazoo River were analyzed for the presence of Hg, Cr, Ni, Pb, Zn, Cu, Cd, and As. Concentrations ranged from <0.01 to 0.50 ppm Hg, <1.0 to 2.3 ppm Pb, 5.0 to 25.0 ppm Zn, and <0.1 to 1.3 ppm Cu (Table 28). Cr, Ni, Cd, and As were not detected above their respective limits of detectability of 0.1, 0.2, 0.1, and 0.5 ppm.

In another Michigan study conducted jointly by the Water Resources Commission, the Fisheries Division of the Department of Natural Resources, and the Michigan Department of Agriculture, fish were sampled during June - July 1971 from 16 inland lake and stream locations in the Lake Michigan basin where metal contamination of sediments had earlier been detected. Fish from four background areas upstream from any municipal or industrial point sources were also collected. Edible

portions of the samples were analyzed for 14 metals including Hg, Cd, Pb, Cr, Ni, Cu, Zn, Mo, Co, Mn, Be, As, V, and Se (see Table 29). Average concentrations detected were 0.3 ppm Hg, 0.1 ppm Cd, 0.2 ppm Pb, 0.2 ppm Cr, 0.2 ppm Ni, 0.7 ppm Cu, 19 ppm Zn, 0.03 ppm Mo, 0.1 ppm Co, 0.5 ppm Mn, 0.003 ppm Be, and 0.106 ppm As. Vanadium and Se were not detected above the sensitivity limit of 0.1 ppm at any of the locations. Five of the samples had mercury concentrations which exceeded the FDA interim guideline of 0.5 ppm. Locations included the Pigeon River, Grand River at Grand Haven, White Lake, and lower Menominee River.

The data show average concentrations of 0.3 ppm Hg, 0.1 ppm Cd, 0.2 ppm Pb, and 0.2 ppm Cr. Nickel was not detected in any of the samples tested. No tolerance limits have been established in the United States for Cd, Pb, Cr, or Ni. Concentrations of Pb appeared high at the Grand River below Jackson and Lansing and in White Lake near Hooker Chemical Company (0.8, 0.9, and 1.3 ppm, respectively). However, the values never approached the Canadian tolerance limit of 10 ppm for Pb. Cd and Cr did not appear significantly higher at the priority locations than the five control stations.

Wisconsin

Mercury determinations were made on fish fillets from 103 locations in Wisconsin including several in the Green Bay area and in Lake Michigan (Kleinert and Degurse, 1971). Mercury levels in fish muscle from sections of the Fox and Menominee Rivers and Green Bay averaged 0.38 ppm. These waters are known to receive wastewaters from pulp and paper mills. Samples from Lake Michigan averaged 0.15 ppm. The authors found that fish samples taken from areas with no known mercury contamination averaged 0.19 ppm (range: 0.01 to 0.6 ppm) and suggest that these values indicate normal background levels of mercury content with both species and size of fish.

DISCUSSION

It appears as of now, that except for mercury, metal residues do not exceed concentrations that are likely to be selected if action levels were to be established. The data are insufficient in quantity, and sampling and analyses have been too variable to permit best use of existing data.

Because metals are magnified in aquatic organisms to much larger concentrations than in the surrounding water, measurement of residues may provide a good sample type to monitor as has been true with DDT. Residues have a distinct advantage over measurement of water concentrations because they more nearly reflect the biologically important fraction of the total metal in the water or sediment.

TRACE METALS IN THE AQUATIC ENVIRONMENT AND HUMAN HEALTH

From the human health standpoint, heavy metals in water are of concern for two reasons. All natural waters contain heavy metals, whether from natural leaching or from man's activities in the watershed. Since many metals are toxic to humans in rather small amounts, the U.S. Public Health Service has established permissible levels of heavy metals for sources to be used for municipal water supplies. Table 30 lists the maximum limits of metals that are allowed in drinking water supplies by the U.S. Public Health Service.

A previously cited study in 1962-63 by the former FWPCA (1968) found cadmium concentrations in the St. Joseph River of 20 ppb, twice the maximum limit recommended for drinking water.

Since 1969, the Michigan Water Resources Commission has sampled for metals in 19 tributaries to Lake Michigan on a monthly basis. Copper and Zinc concentrations were always well below the recommended limits. One value of 20 ppb for cadmium in the Kalamazoo River did exceed the U.S. Public Health Service drinking water standard. Hexavalent chromium was found in about 11 percent of the samples taken, and was often in excess of the 50 ppb drinking water standard. The positive values averaged 69 ppb with a high of 150 ppb in the Grand River. Lead concentrations of 50 ppb were measured in the Grand and Manistee Rivers. These values equal the drinking water standard of 50 ppb. Because of ongoing state and Federal programs of pollution abatement, the occasional values which exceed drinking water standards will probably not be found in the future.

The second concern to human health from metals arises because metals can accumulate to high levels in the tissues of aquatic organisms important as human food. In food products, the U.S. Food and Drug Administration has established levels for some substances which they consider safe for human consumption. Fish or other food products exceeding these action levels are banned from the market and considered unsafe for human consumption. The FDA has placed a 0.5 ppm action level for mercury. Closure of many areas to commercial fishing has resulted from this action level. No other action levels have been established for metals in fish, however.

Canadian Officials, who also use the 0.5 ppm Hg limit, have set tolerance limits for four other metals in marine and freshwater animal products:

Metal	Permissible Limit (ppm)
Arsenic	5
Lead	10
Copper	100
Zinc	100

Limited data cited previously on metals in fish indicates that except for mercury, metal residues presently found in fish do not exceed concentrations that are likely to be selected by the U.S. FDA if action levels were established.

While human health is of the utmost importance, even more sensitive to metals in the aquatic ecosystem are the organisms that live their entire lives there.

TOXICITY OF TRACE METALS TO AQUATIC ORGANISMS

Many metals are found in organisms and it is known that some are required in certain bodily processes. Hemoglobin, that part of the blood which carries oxygen to the tissues, contains iron in an organic complex. Some invertebrates have hemocyanin instead of hemoglobin to transport oxygen to tissues. In hemocyanin, copper takes the place of iron. Copper also appears necessary for the synthesis of hemoglobin, and both iron and copper function in oxidative enzymes which yield energy in the body. Metals such as zinc, cobalt, manganese, and magnesium are found in compounds with enzymatic actions and some are important components of vitamins, necessary for the proper maintenance of bodily functions and growth. Still other metals are often present but their function remains unknown. Some metals not essential to organisms are known to be toxic even at very small concentrations. These include mercury, cadmium, arsenic, antimony, barium, bismuth, lead, selenium, beryllium, and silver. An excess of essential metals causes physiological imbalances and is toxic.

Much of the metal toxicity work that has been done on aquatic organisms is of an acute or short term nature (often a week or less). The endpoint of most of these bioassays is mortality. While knowing levels that can kill is important to proving the cause of a fish kill or in assessing the immediate impact of an accidental discharge of a metal-bearing waste, the concentration of a metal that can be toxic to aquatic organisms over a long period is of most concern to the maintenance of a healthy, well-balanced population. Chronic or extended exposure to concentrations of metals much lower than the lethal level can have serious, though perhaps more subtle, adverse affects on the biota. Metals accumulate in tissues and organs gradually and build to a point where they may cause physiological impairment. These levels can have direct effects on organisms by causing a decrease in the growth rate or by impairing their reproduction. Indirectly, the metals may weaken the species, making it more vulnerable to other environmental stresses. A concentration of some other substance that alone would not be harmful might act additively or synergistically with the metal in the water and result in mortality or in other inimical effects. Changes in other factors such as temperature and pH can stress the animal and can also alter the form of a metal, possibly changing non-toxic metal compounds into toxic ones. The stress caused by the metal can also make the species more vulnerable to overcrowding or predation.

Different animals vary in their sensitivities to heavy metals and different life stages of a species may vary in sensitivity also. A species more stressed by the metal might succumb to predators at a higher rate than natural. A change in the population structure in the aquatic environment would result when a species more tolerant of heavy metals filled the niches formerly held by more sensitive species.

This shift in species dominance might be good or bad from man's standpoint, but the important point is that the ecological balance of the natural community has been upset.

Metals also exert an indirect influence on a species if it kills or reduces in abundance the food chain organisms. Some fish fry are known to be very specific in their food requirements when they first begin to feed. Siefert (1972) has found that for yellow perch, the first food is Polyarthra, a rotifer, and copepods; for bluegills, Polyarthra; emerald shiners, rotifers and copepod nauplii (young); and rainbow smelt-Cyclops and copepod nauplii. It seems probable that other species of fish are also very specific in food requirements when they first begin to feed. Not much is known about the relative sensitivities of these invertebrates to metals, but it seems likely that they would in some cases be more sensitive than the fish. Thus, if a metal eradicates an invertebrate species necessary as the first-food for a fish species, that fish species will be eliminated even though the metal concentration was not high enough to produce a direct effect on the fish.

Many factors can influence the toxicity of heavy metals. Other ions in the water can combine with metallic ions and cause the metals to precipitate; not much is known about the toxicity of these precipitated compounds; however, changes in pH or temperature may cause precipitates to redissolve. Water hardness affects metal toxicity markedly. Pickering and Henderson (1964) found that the acute toxicity of nickel, cadmium, copper, lead, chromium, and zinc decreased as water hardness increased; Mount (1968) and Mount and Stephan (1969) showed that the chronic toxicity of copper to fathead minnows was greater in soft water than in hard water. Mount has also suggested the use of an application factor for predicting chronically safe levels where only acute data is available. This basic approach has been widely used, especially in the book entitled Water Quality Criteria prepared by the U. S. Department of the Interior. Table 31 lists the toxicity of various heavy metals to fish and invertebrates found in or similar to ones found in Lake Michigan as well as important species of freshwater algae.

In order to estimate safe levels using the application factor approach, both the acute toxicity of a pollutant to locally important species is needed and an estimate of the absolute value of the factor. It is preferable to have an estimate based on experimental data but in the absence of such data, an arbitary value of 1/100 is recommended. This 1/100 value is derived as an average of application factor values for those metals for which experimental data is available. It is important to remember that application factors are not safety factors but rather can be used to calculate levels that are just safe. Normally, 96-hour TLM tests are required on locally important fishes (of fingerling age) in the water of concern and with the pollutants of concern. Surprisingly, data on the acute toxicity of metals using

Lake Michigan water and fish are not available. However, it is possible to estimate the probable safe ranges using existing bioassay data to estimate the 96-hour TLM values for Lake Michigan fish and water. This requires subjective extrapolations but estimates so derived will be reasonably close to reality. Two important cautions are that the factors are not yet applicable to organisms other than fish and the presence of biologically inactive forms of the metals will introduce error.

Of the fish species in Lake Michigan, the salmonids, minnows, and the catfish are much more sensitive to the metals than perch, walleyes, and sunfish (such as smallmouth bass and bluegills). Therefore, toxicity data for salmonid and minnow fingerlings should be used for estimating probable safe concentrations. The zooplankton organisms are also sensitive if Daphnia magna has representative sensitivity. In general, algae are not any more sensitive than sensitive fishes. Following are the probable safe ranges of various metals based on data in Table 31 and utilizing the application factor approach:

Copper

Application factors have been determined for fathead minnows and brook trout and gave an estimate for the factor of 1/12. Using data for fingerlings, and adjusting TLM values for the hardness in Lake Michigan, the probable 96-hour TLM value is approximately 50 to 100 µg/l and this times 1/12 is about 4 to 8 ppb - an estimate of the probable safe range. These estimates appear to be low enough to protect Daphnia and benthic invertebrates also.

Nickel

Only one estimate of the application factor, based on fathead minnows, is available and that is 1/30. There is so little acute data that estimating the 96-hour TLM for Lake Michigan water and fish is difficult - but from the rainbow trout and fathead data in Table 31, 20 mg/l appears reasonable and this times 1/30 gives a probable safe concentration estimate of approximately 700 µg/l. This value is too high for Daphnia magna. Until data show otherwise, this should be lowered to 50 - 100 µg/l to insure protection of zooplankton.

Zinc

Only one application factor estimate using fathead minnows is available and gave a value of 1/100. The 96-hour TLM values appear to be approximately .2 to 1 mg/l and this times 1/100 gives 2 to 10 µg/l as an estimated probable safe range, apparently low enough for all animals so far tested.

Cadmium

Work by Eaton (1971) on bluegills and by Pickering and Gast (1971) shows that short term toxicity tests on eggs and fry give a better estimate of safe concentration than the application factor. From the salmonid fry data in Table 31, a concentration of 1-5 µg/l is probably safe except for Daphnia magna. There is no known data for zooplankton organisms common to Lake Michigan.

Chromium

Application factors for fatheads and brook trout have been determined and were 1/30 and 1/90 respectively. Chromium toxicity is little affected by hardness.

The best estimate of the probable safe concentration available now is the one experimentally safe for brook trout - 200 µg/l. Algae are more sensitive according to some data, but since the U. S. Public Health Service drinking water limit is 50 µg/l, this value should be used for Lake Michigan.

Unpublished work of Pickering (Newtown Fish Toxicology Laboratory, National Water Quality Laboratory) on trivalent chromium in life cycle tests indicates that both forms of chromium are about equally toxic. Therefore, the above recommended level should apply to total chromium.

Other Metals

Estimates of safe concentrations for other metals must be based on 1/100 of the 96-hour TLM until data is available upon which better predictions can be made. Such data is continually being developed and more will be available in the near future. It is somewhat surprising that acute toxicity data (96-hour TLM) for metals using Lake Michigan water and fish are not available. Hopefully publication of the report will provide the stimulus needed for one or more laboratories to conduct these relatively simple but very important studies.

FIGURE 1 WATER CONCENTRATIONS OF ZINC IN THE OPEN LAKE.

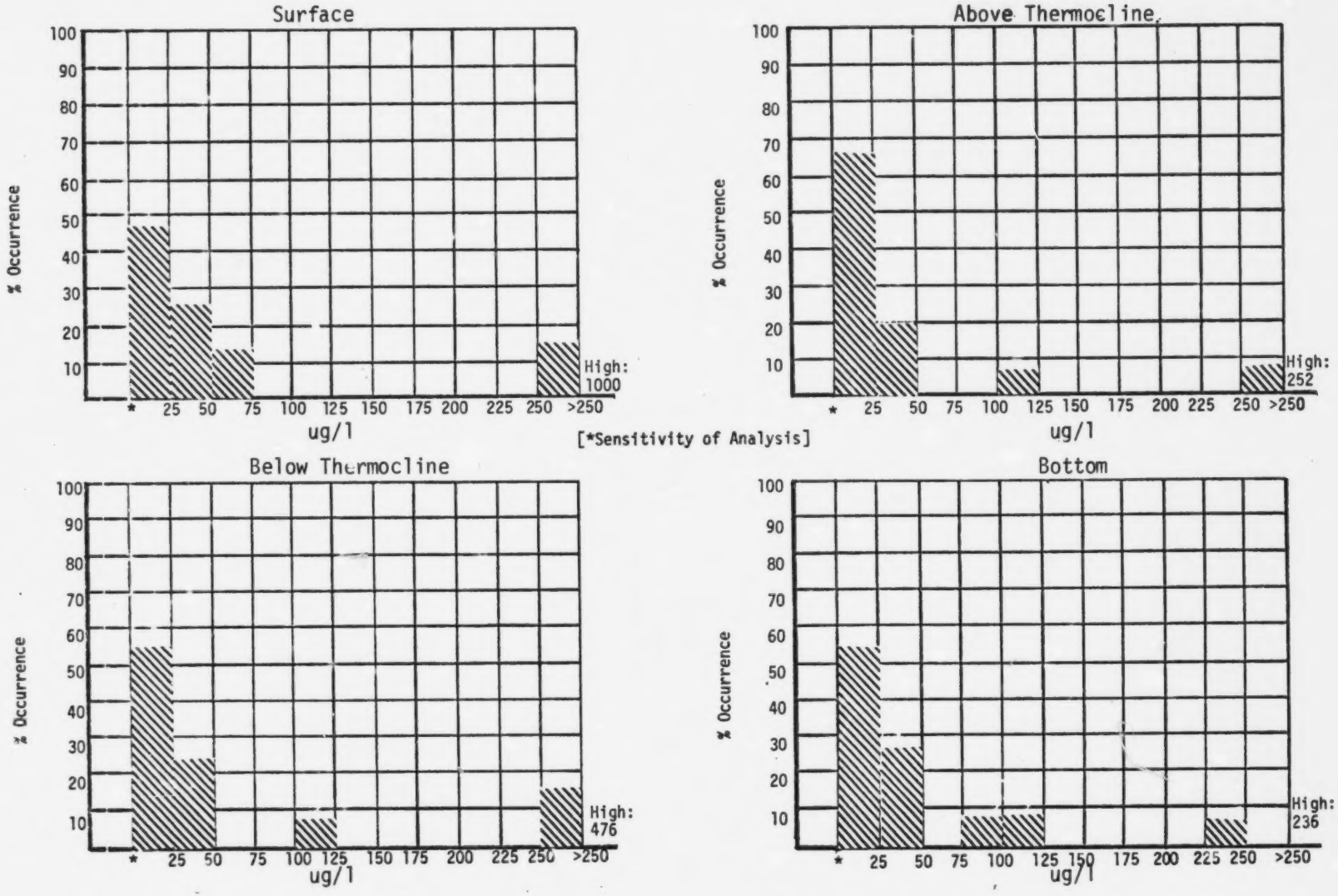


FIGURE 2 WATER CONCENTRATIONS OF FOUR METALS IN INSHORE AREAS OF SOUTHERN LAKE MICHIGAN (BASED ON 24 SAMPLES).

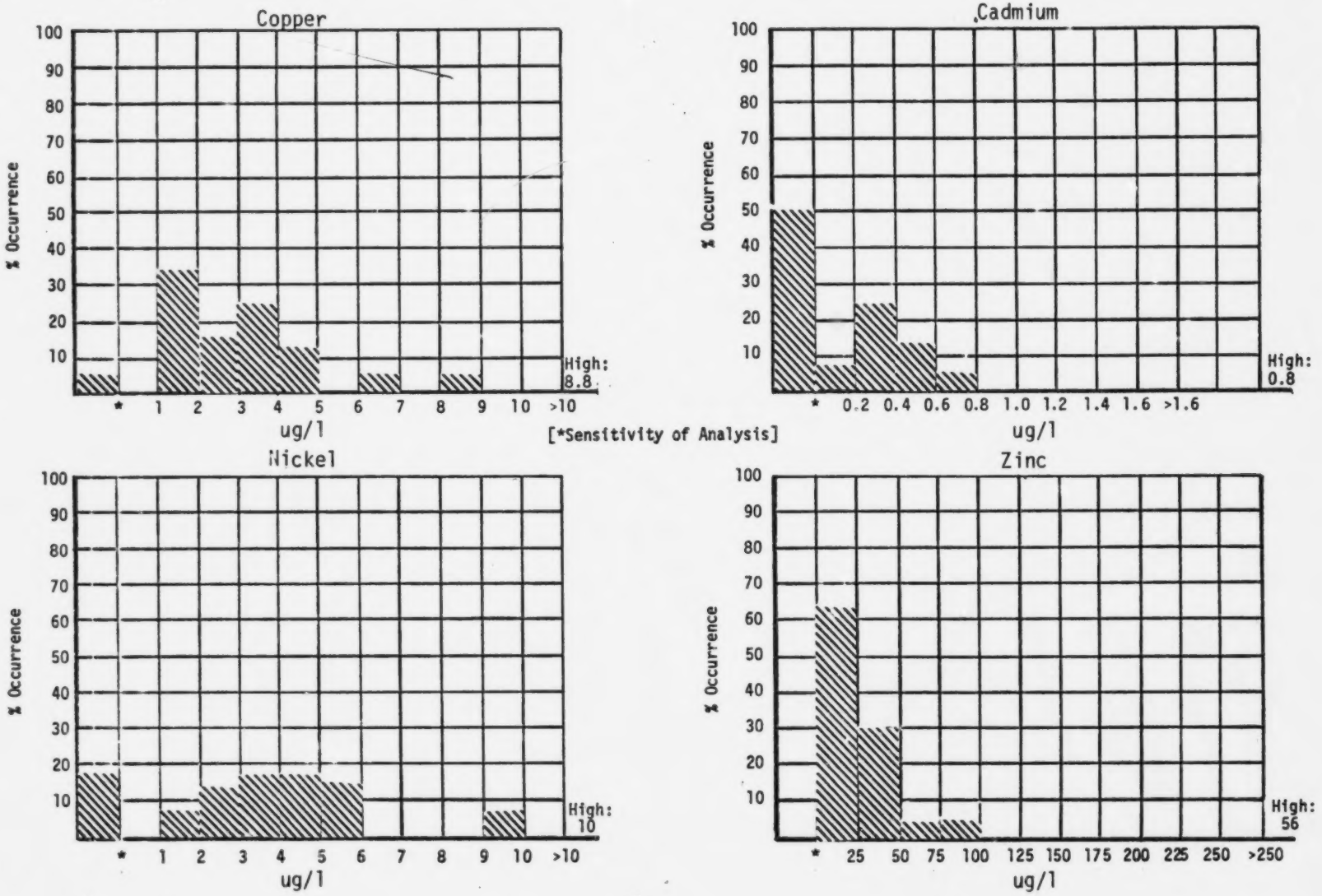


FIGURE 3 WATER CONCENTRATIONS OF FOUR METALS FROM INSHORE AREA AT GREEN BAY (BASED ON 18 SAMPLES).

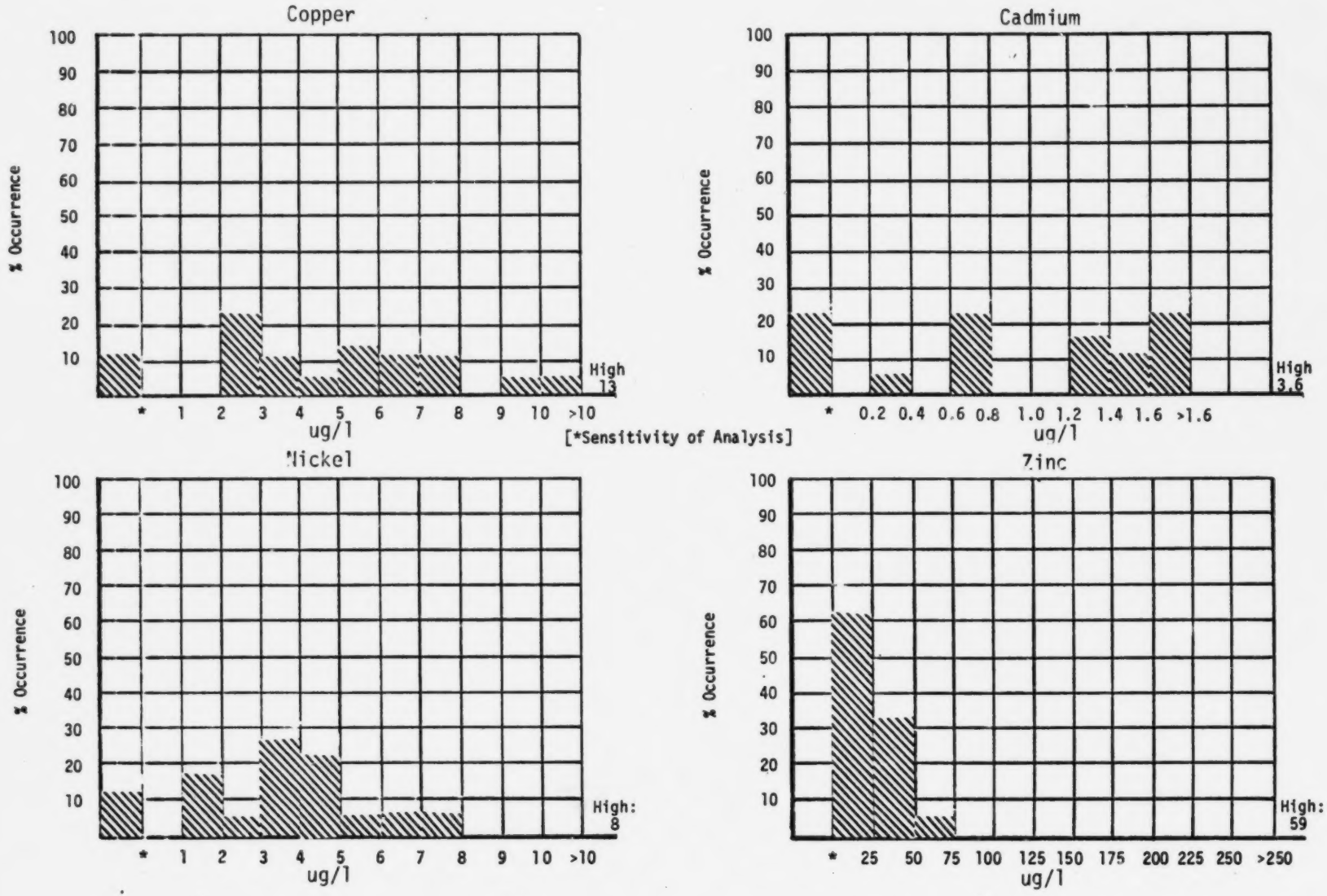
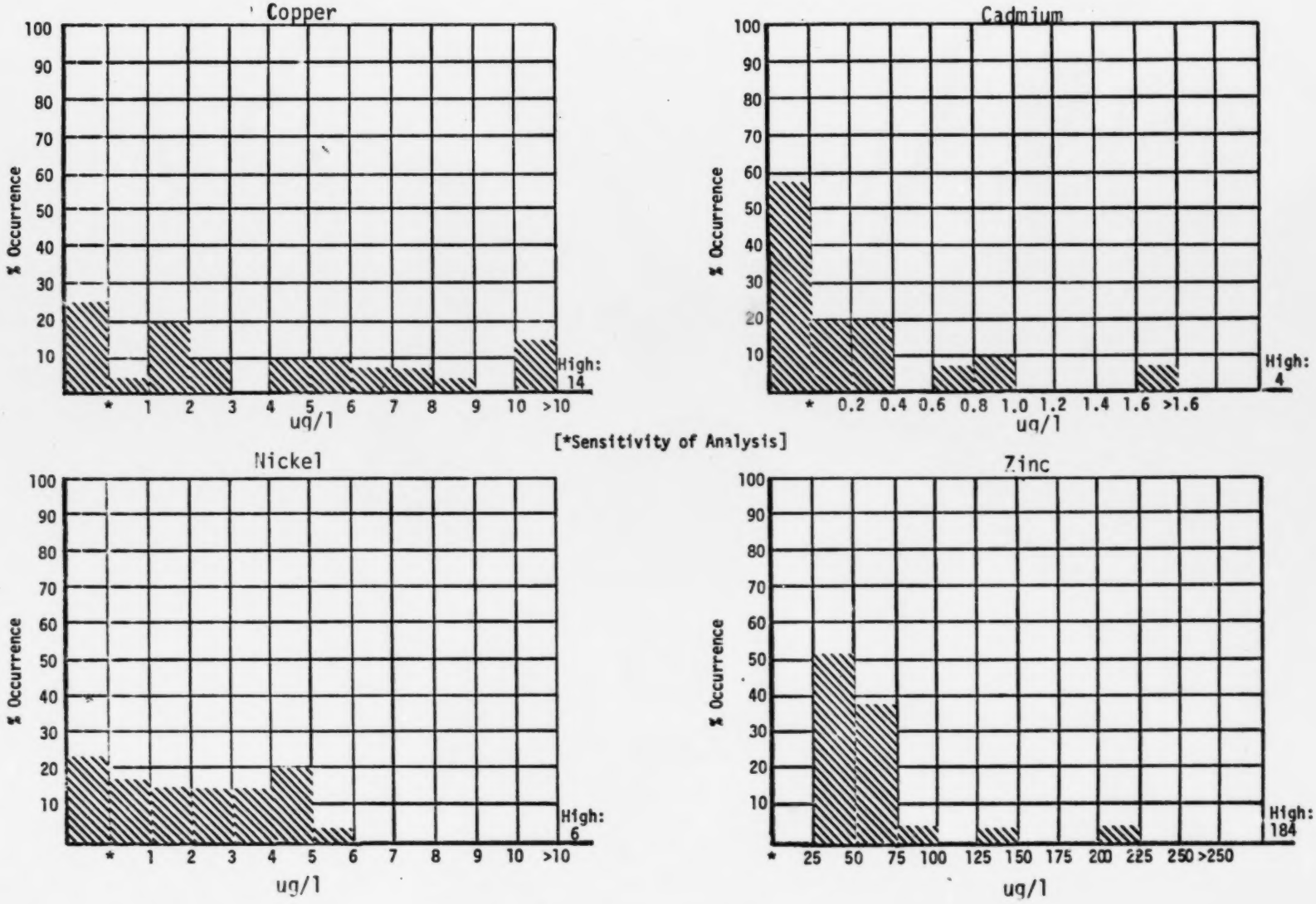


FIGURE 4 WATER CONCENTRATIONS OF FOUR METALS FROM INSHORE AREAS OF NORTHEASTERN LAKE MICHIGAN (BASED ON 31 SAMPLES).



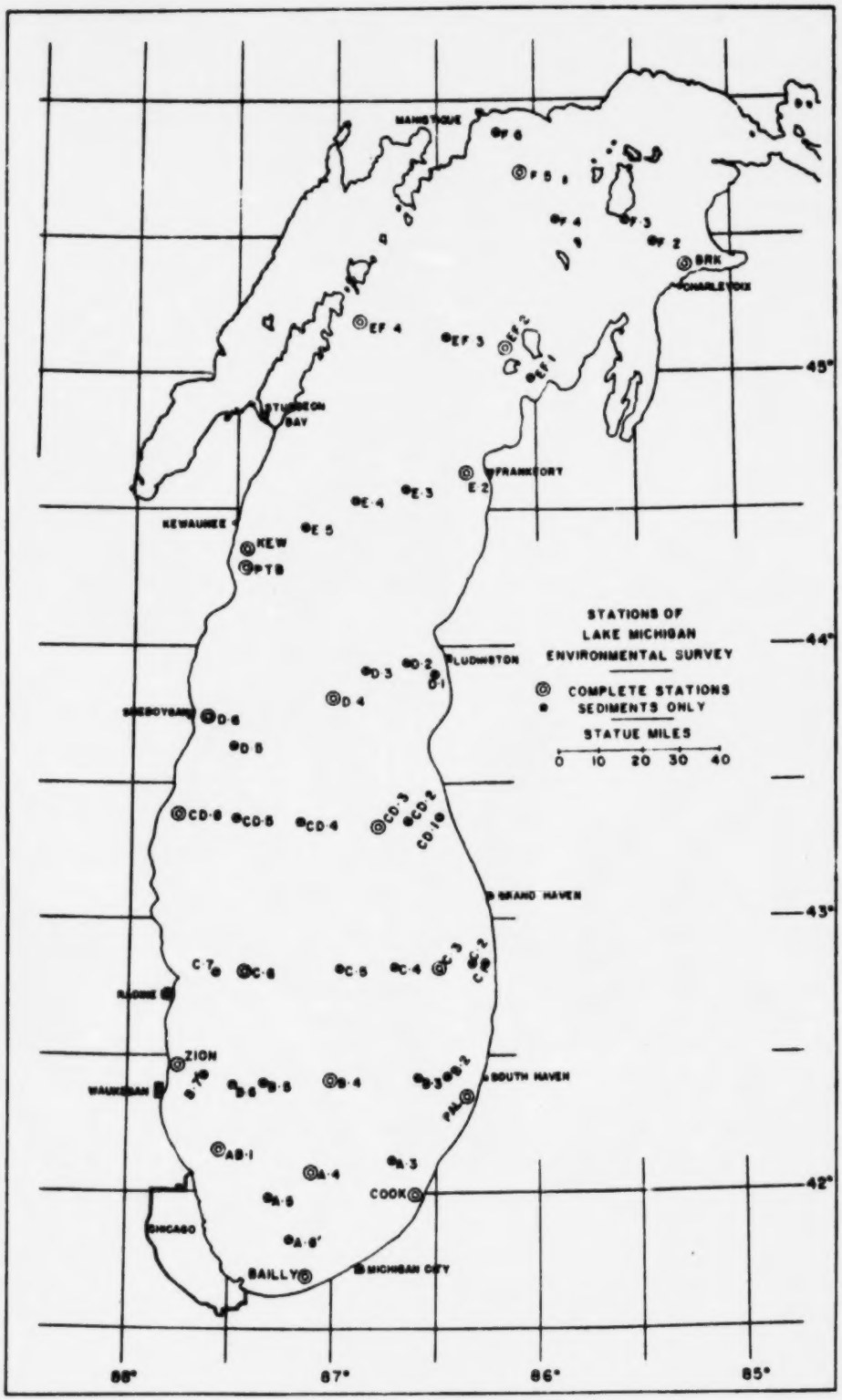
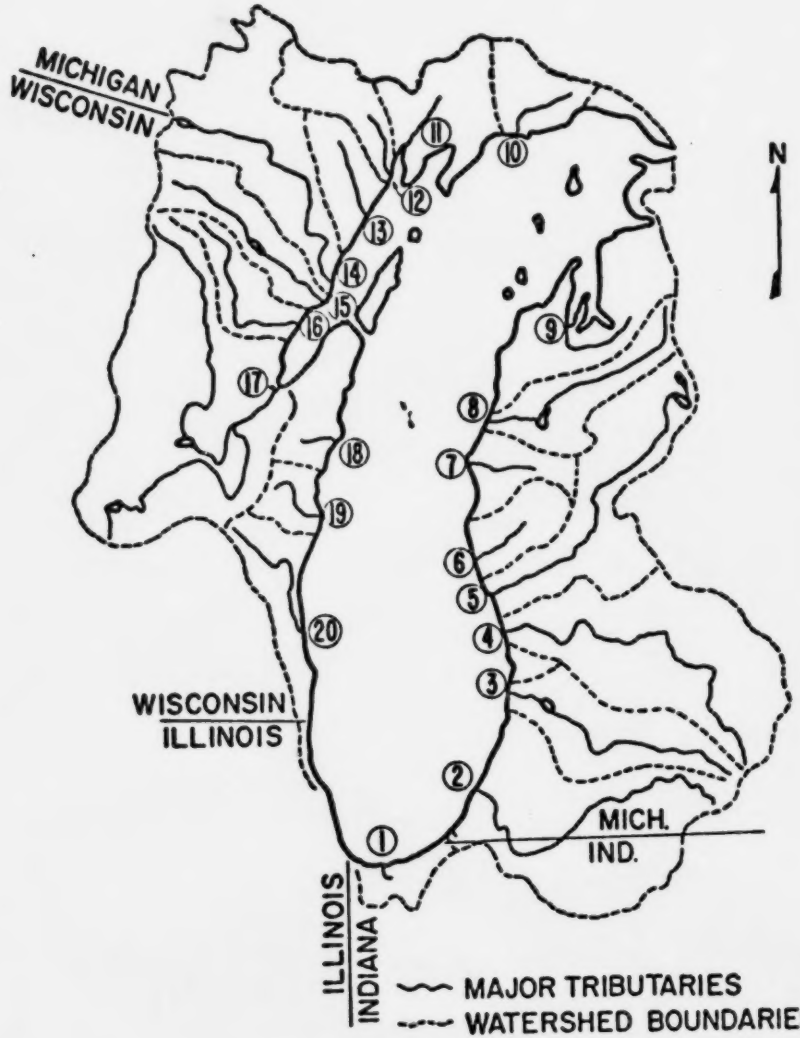

MANISTIQUE
BRK
CHARLEVOIX
STURGEON BAY
FRANKFORT
KEWAUNEE
KEW
PTB
LUDINGTON
SHEBOYGAN
GRAND HAVEN
ZION
WAUKEGAN
SOUTH HAVEN
PAL
COOK
CHICAGO
BAILLY
MICHIGAN CITY
STATIONS OF
LAKE MICHIGAN
ENVIRONMENTAL SURVEY
COMPLETE STATIONS
SEDIMENTS ONLY
STATUE MILES
0 10 20 30 40
45°
44°
43°
42°
88°
87°
86°
85°

FIGURE 5

FIGURE 6 LAKE MICHIGAN'S MAJOR TRIBUTARIES AND WATERSHED BOUNDARIES. ADAPTED FROM U.S. DEPARTMENT OF THE INTERIOR (1968).



KEY	RIVER	DRAINAGE AREA (sq. mi.)	MEAN DISCHARGE (cfs)
(1)	BURNS DITCH	280	130
(2)	ST. JOSEPH	4590	3400
(3)	KALAMAZOO	2030	1300
(4)	GRAND	5570	3360
(5)	MUSKEGON	2780	1900
(6)	WHITE	480	370
(7)	P. MARQUETTE	770	610
(8)	MANISTEE	2010	2100
(9)	BOARDMAN	350	190
(10)	MANISTIQUE	1450	1700
(11)	WHITEFISH	315	-
(12)	ESCANABA	920	900
(13)	FORD	470	320
(14)	MENOMINEE	4150	3100
(15)	PESHTIGO	1160	830
(16)	OCONTO	930	570
(17)	FOX	6440	4140
(18)	MANITOWOC	440	-
(19)	SHEBOYGAN	440	230
(20)	MILWAUKEE	850	380

FIGURE 7 WATER CONCENTRATIONS OF FOUR METALS IN INDIANA HARBOR CANAL (BASED ON 58 SAMPLES)

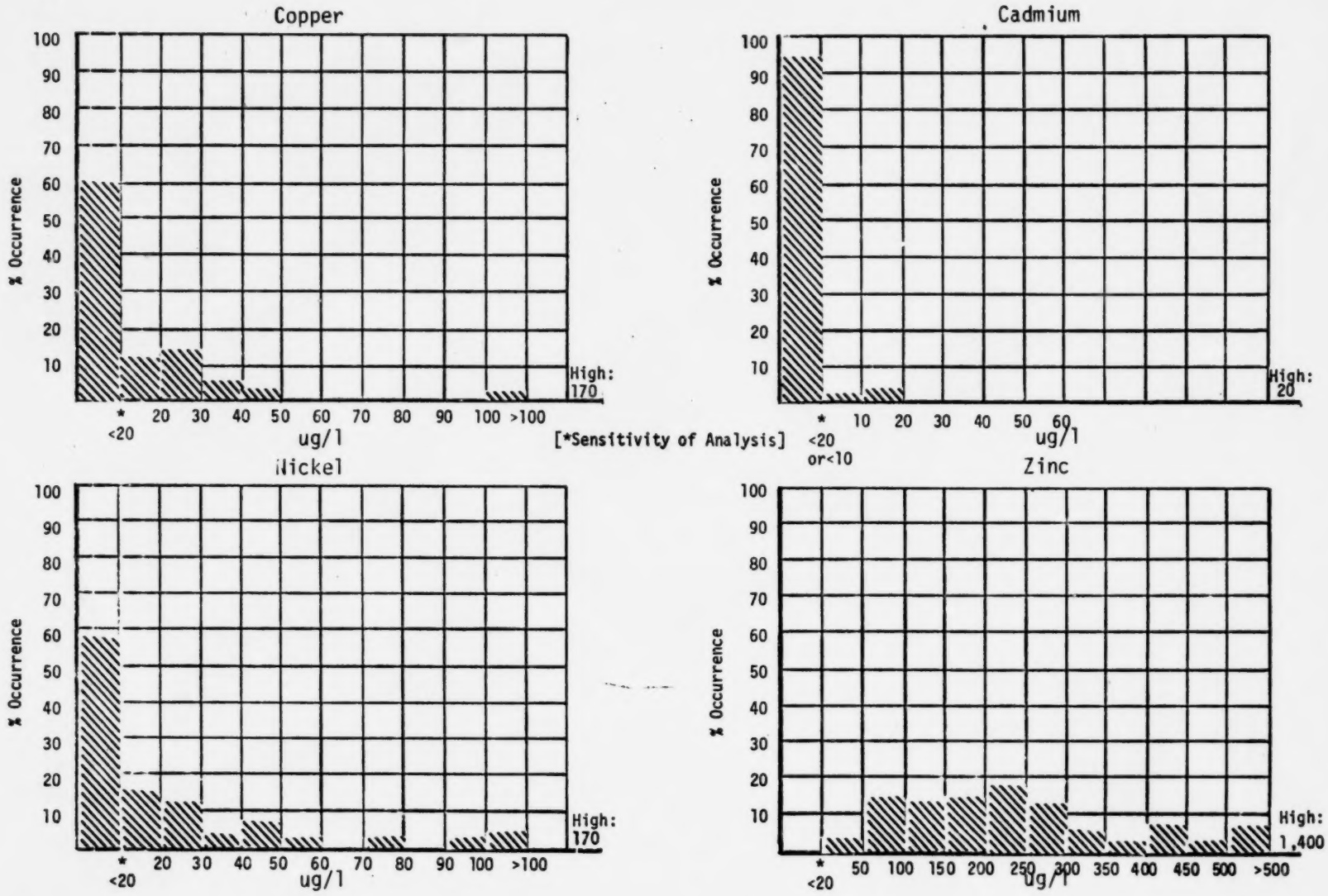


FIGURE 8 WATER CONCENTRATIONS OF LEAD IN THE INDIANA HARBOR CANAL (BASED ON 58 SAMPLES).

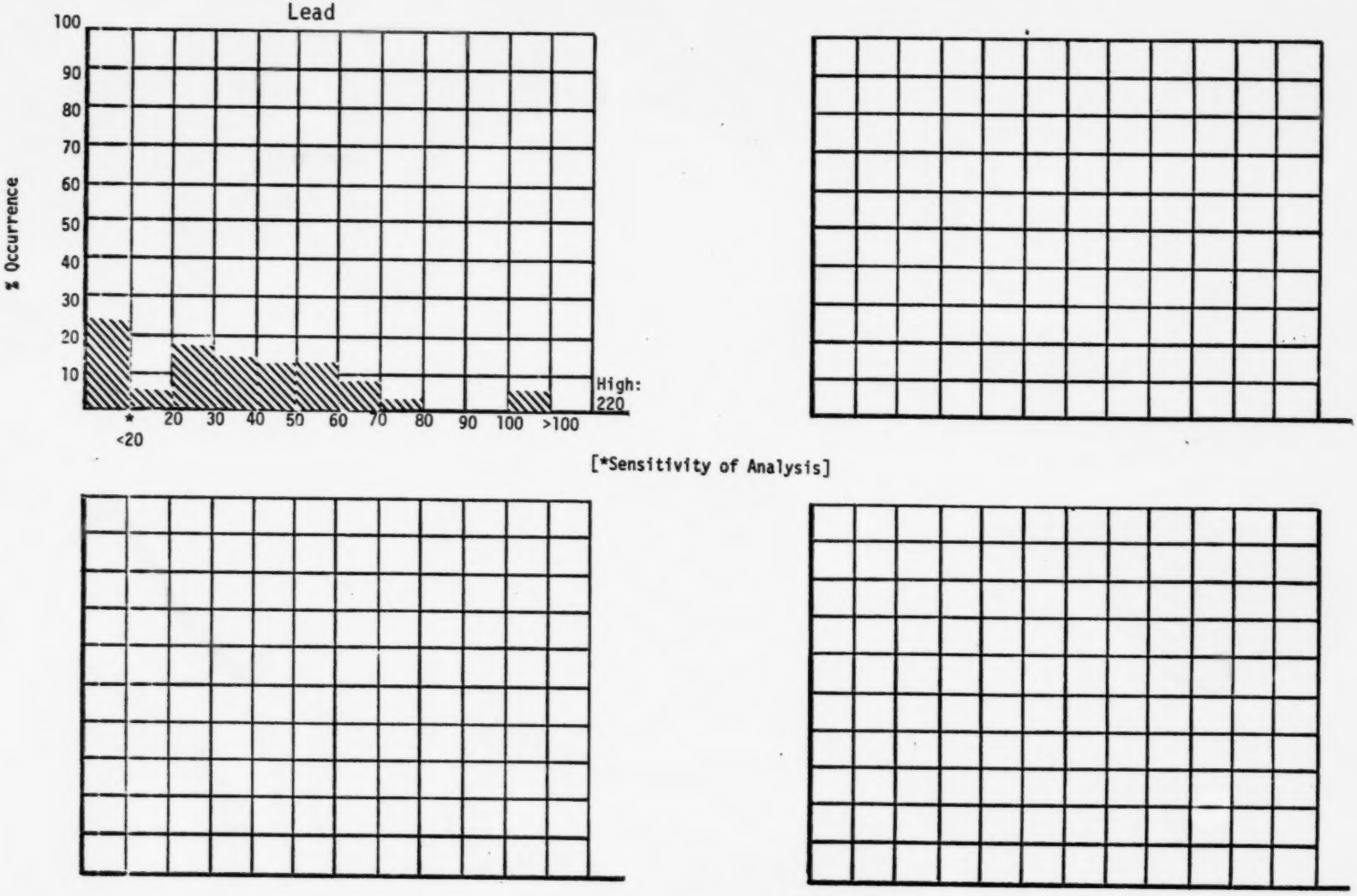


FIGURE 9 WATER CONCENTRATIONS OF FOUR METALS IN TRAIL CREEK, INDIANA (BASED ON 58 SAMPLES).

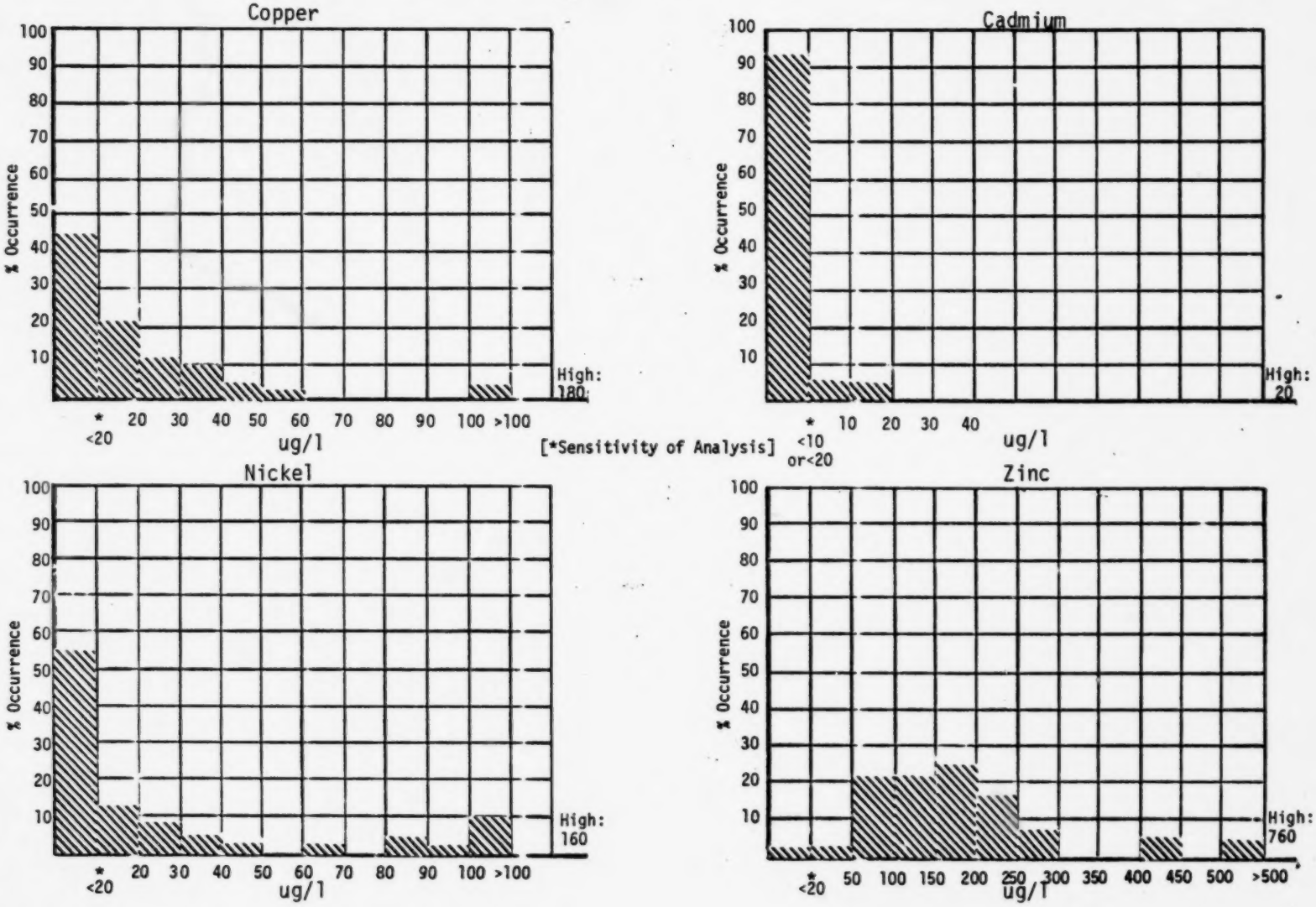


FIGURE 10 WATER CONCENTRATIONS OF LEAD IN TRAIL CREEK, INDIANA (BASED ON 58 SAMPLES).

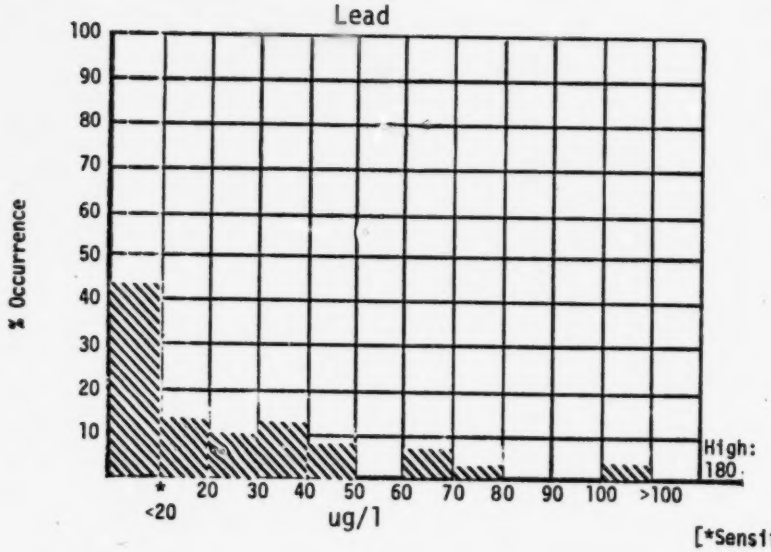


FIGURE 11 WATER CONCENTRATIONS OF FOUR METALS IN BLACK RIVER AT SOUTH HAVEN, MICHIGAN (BASED ON 15 SAMPLES).

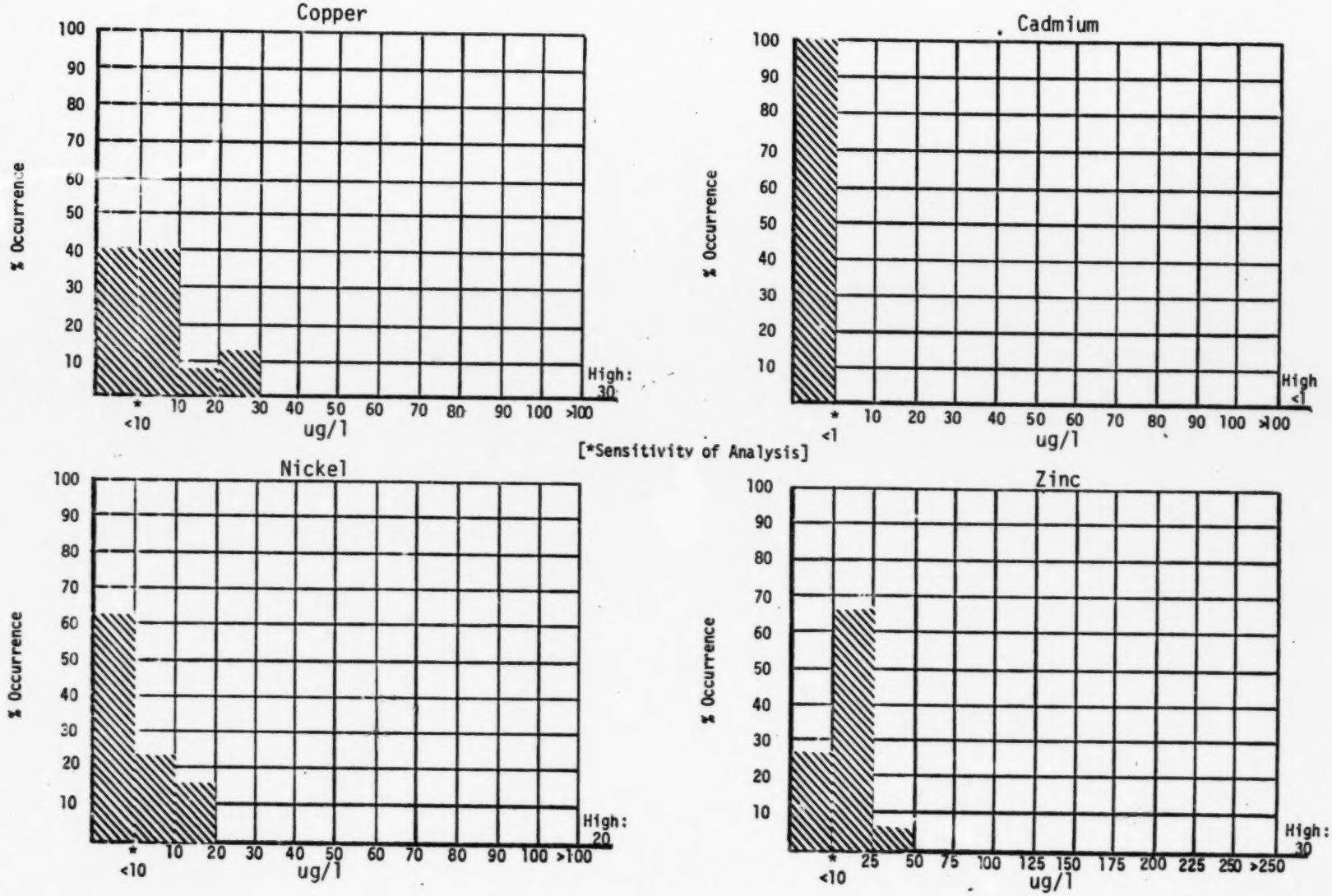


FIGURE 12 WATER CONCENTRATIONS OF FOUR METALS IN BLACK RIVER AT HOLLAND, MICHIGAN (BASED ON 15 SAMPLES).

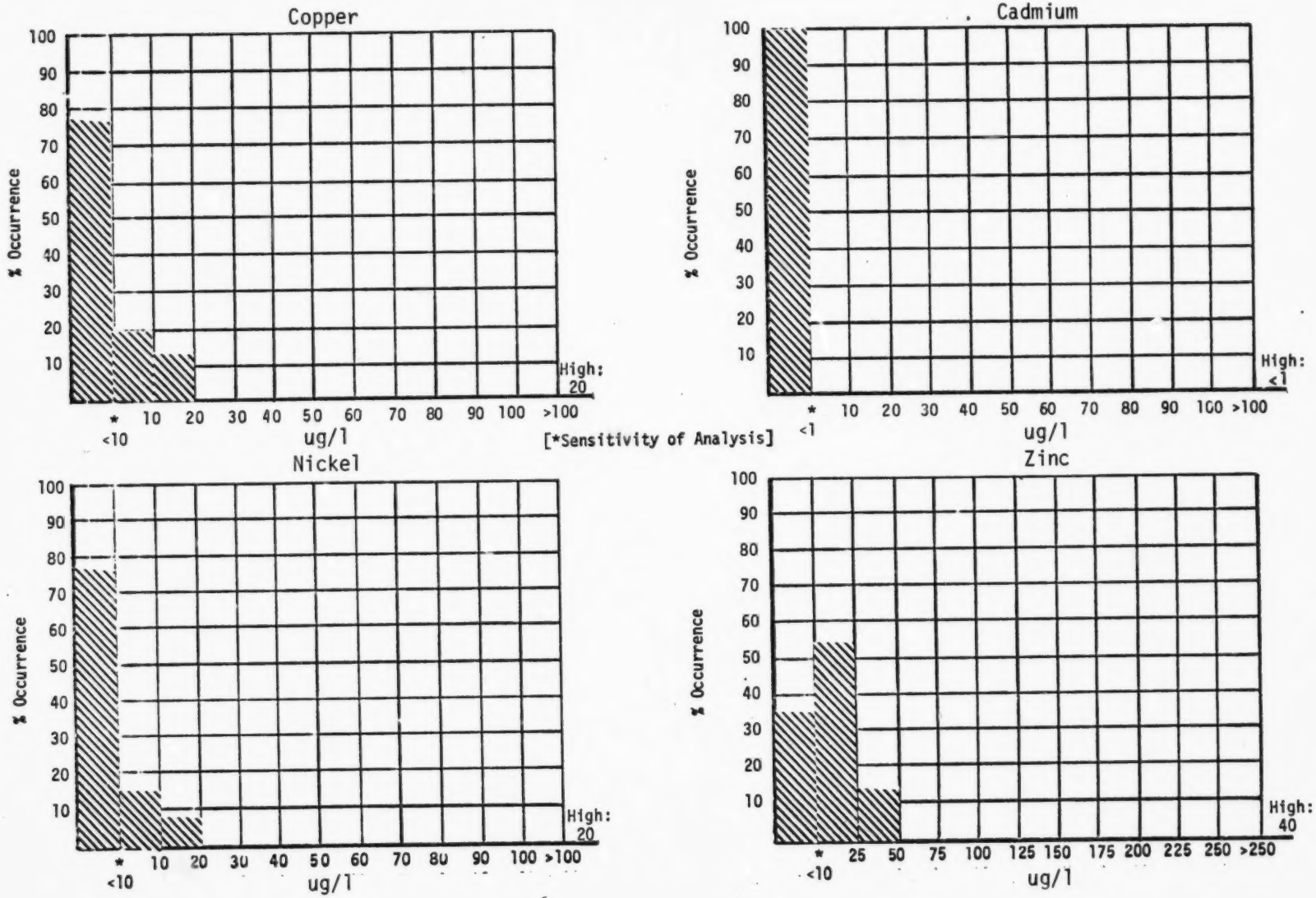


FIGURE 13 WATER CONCENTRATIONS OF FOUR METALS IN GRAND RIVER AT GRAND HAVEN, MICHIGAN (BASED ON 16 SAMPLES).

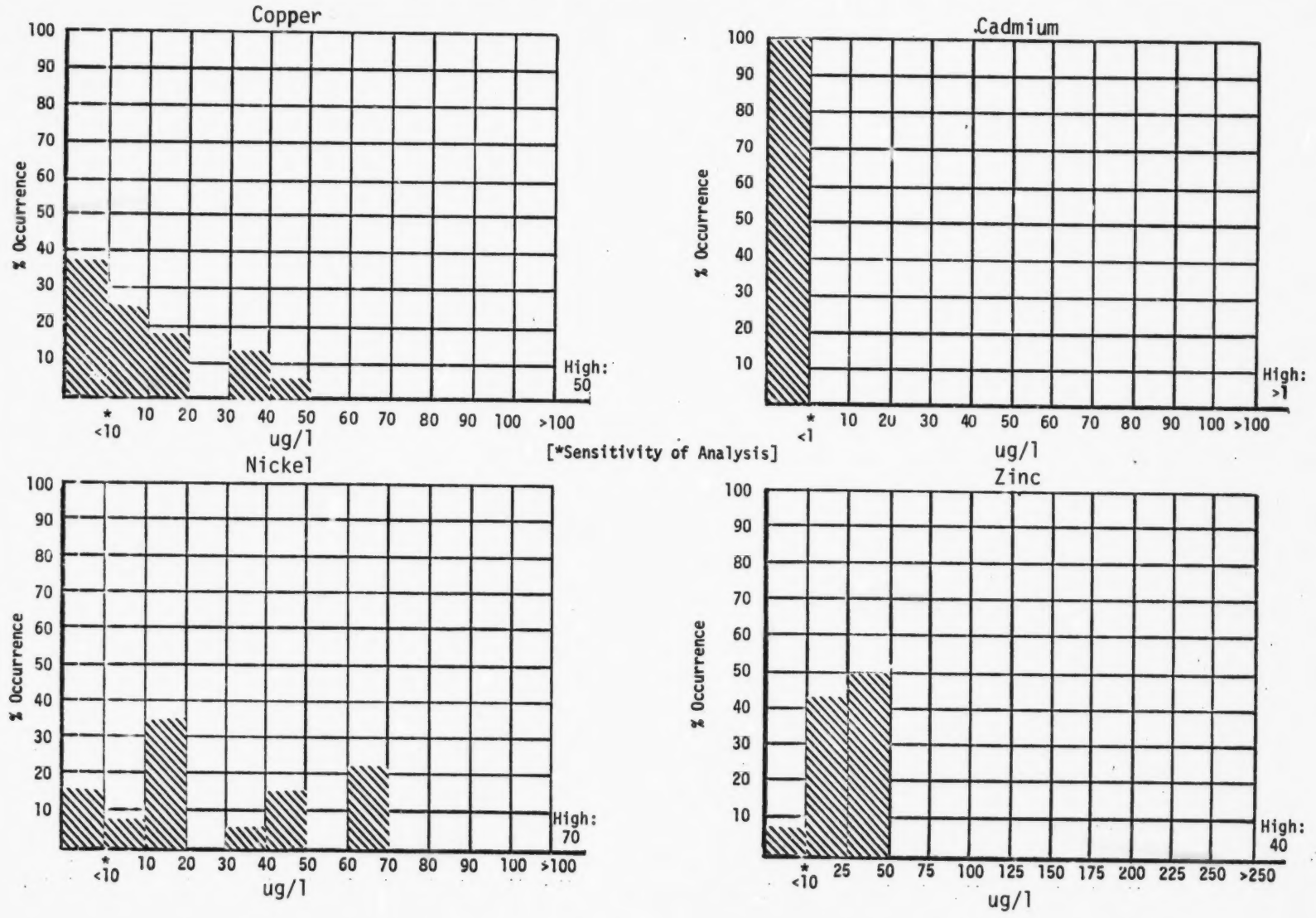


FIGURE 14 WATER CONCENTRATIONS OF FOUR METALS IN MENOMINEE RIVER, MICHIGAN (BASED ON 15 SAMPLES).

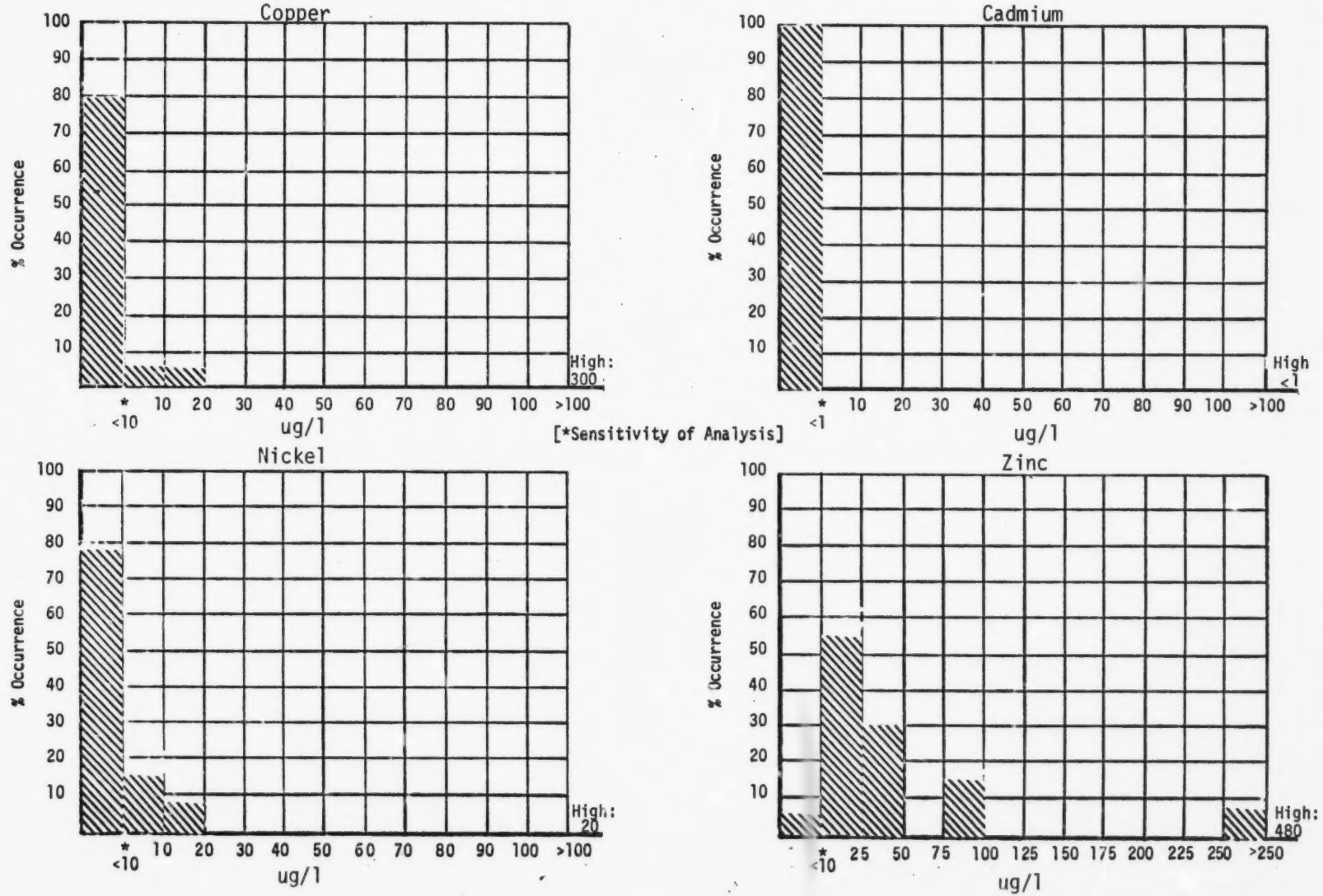


FIGURE 15 WATER CONCENTRATIONS OF FOUR METALS IN ST. JOSEPH RIVER (BASED ON 18 SAMPLES).

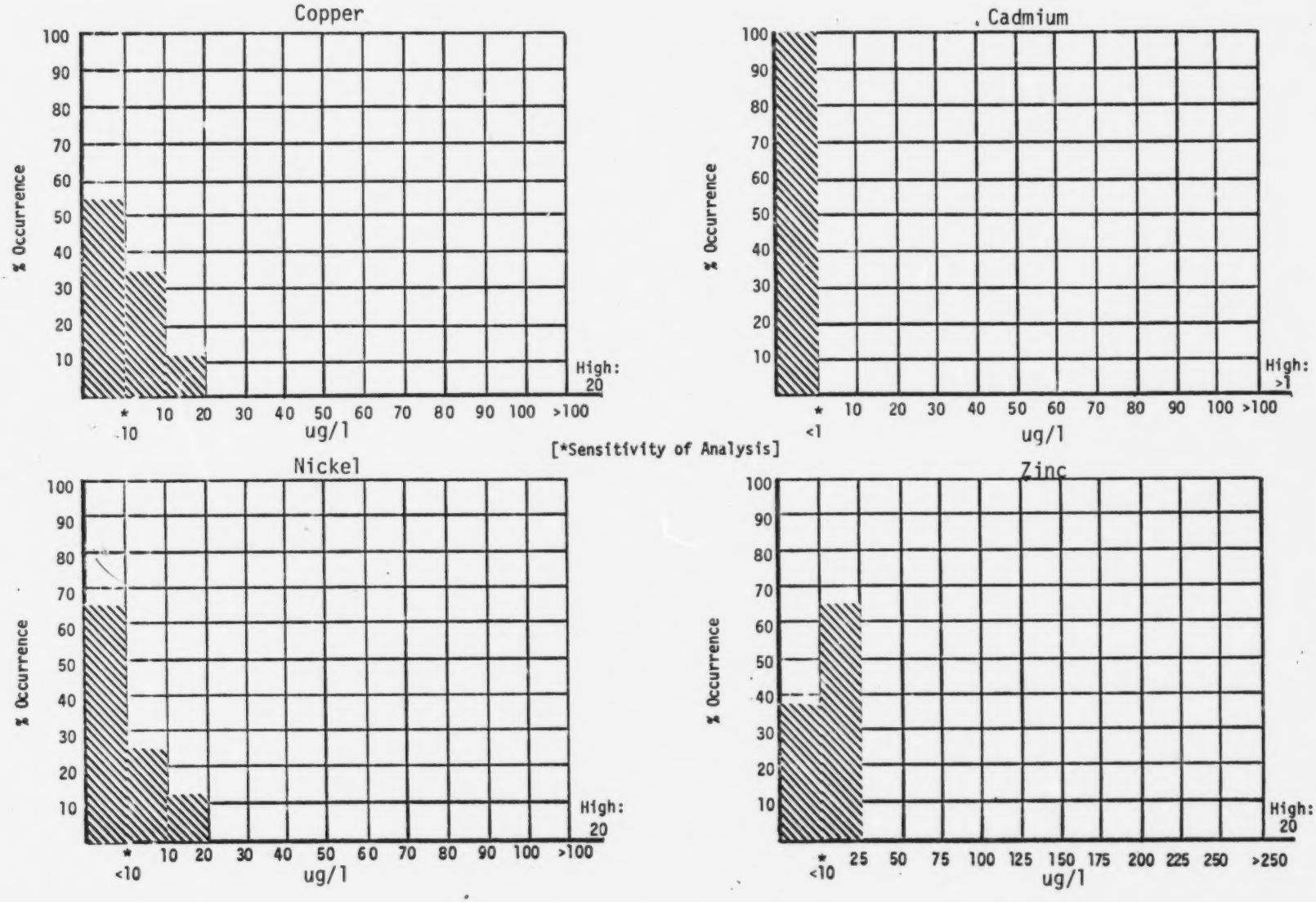
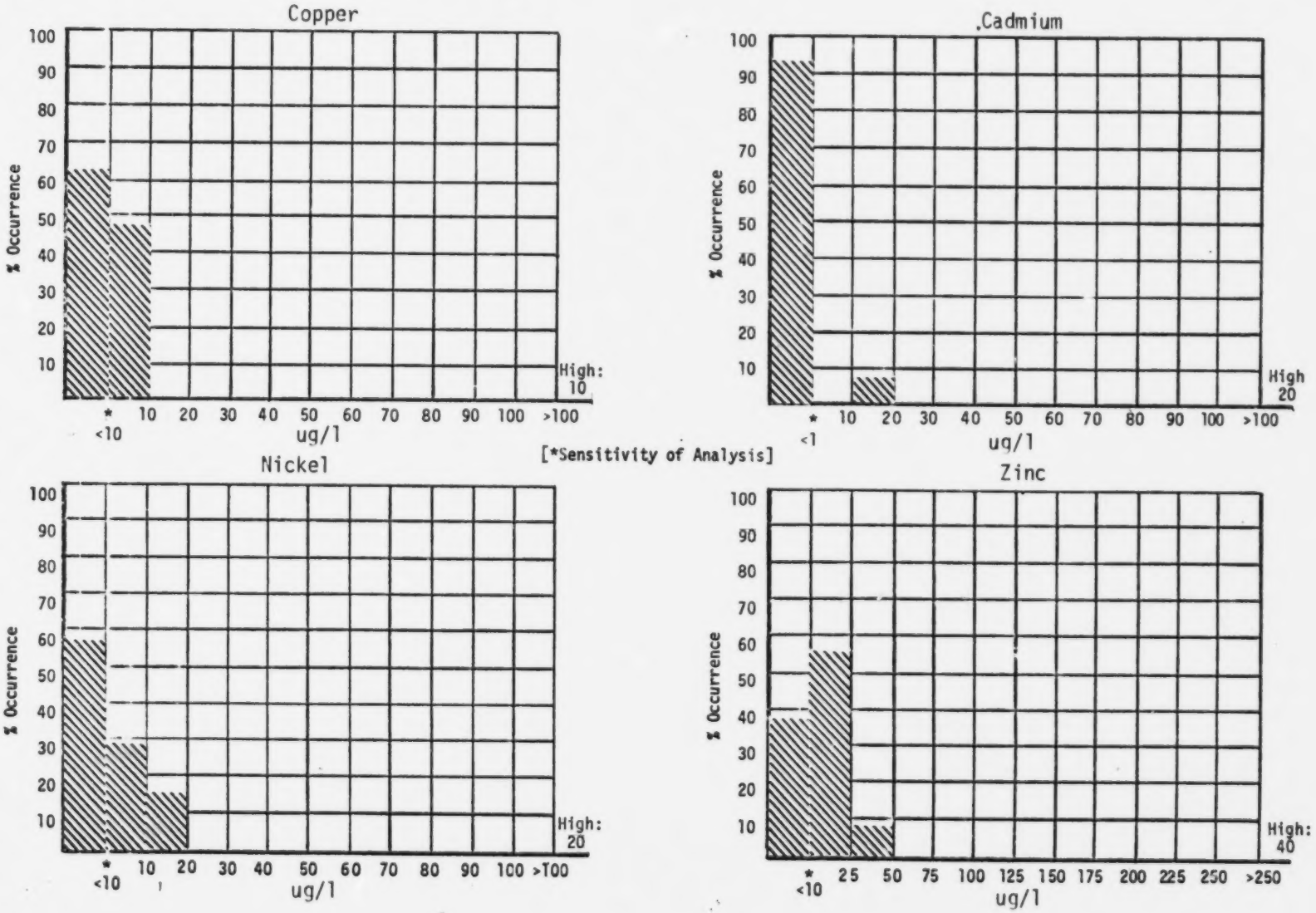


FIGURE 16 WATER CONCENTRATIONS OF FOUR METALS IN KALAMAZOO RIVER, MICHIGAN (BASED ON 16 SAMPLES).



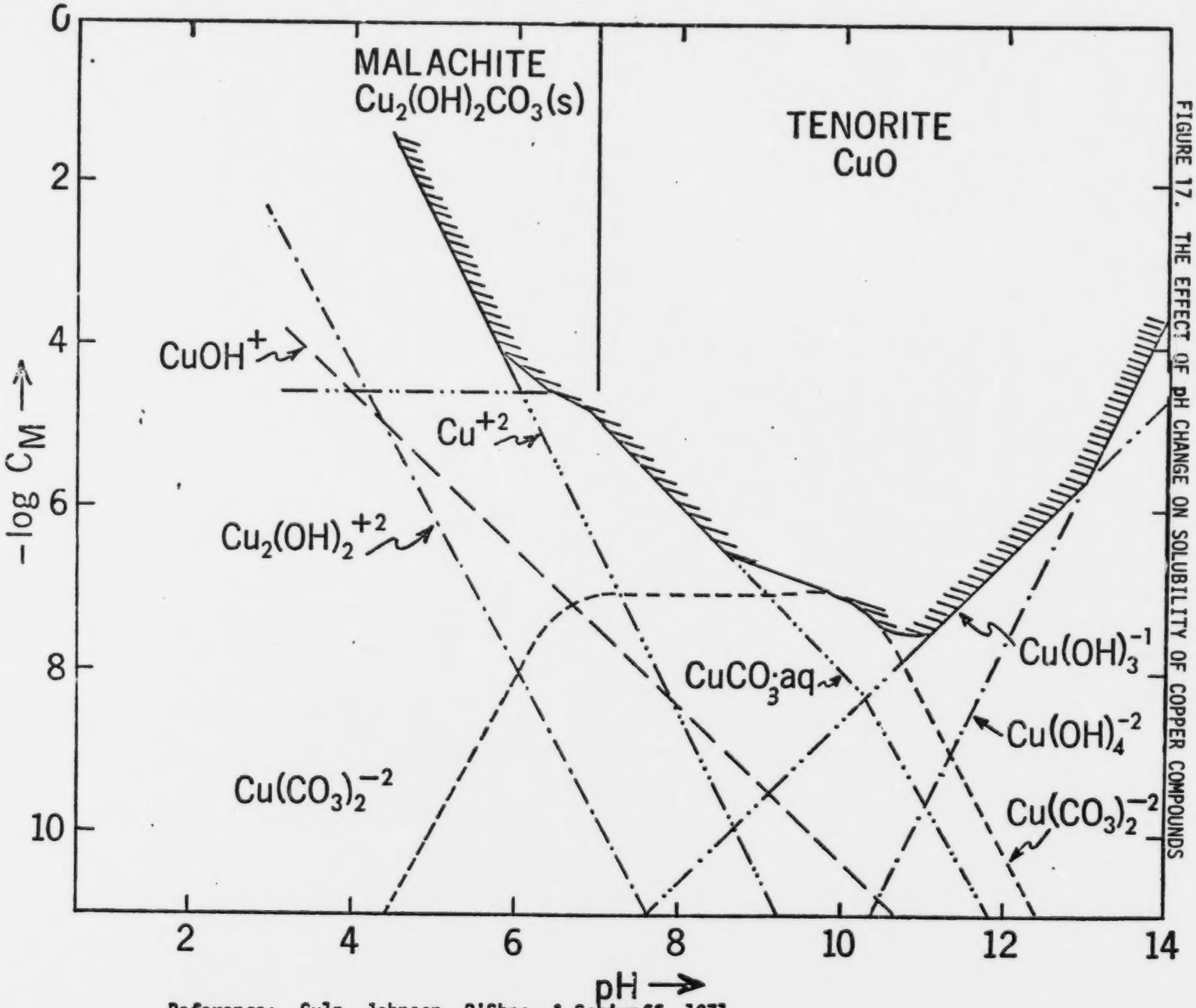


FIGURE 17. THE EFFECT OF pH CHANGE ON SOLUBILITY OF COPPER COMPOUNDS

Reference: Culp, Johnson, O'Shea, & Schimpff, 1971.

FIGURE 18. FISH COLLECTION LOCATIONS IN THE GRAND RIVER BASIN FOR HEAVY METALS ANALYSIS.

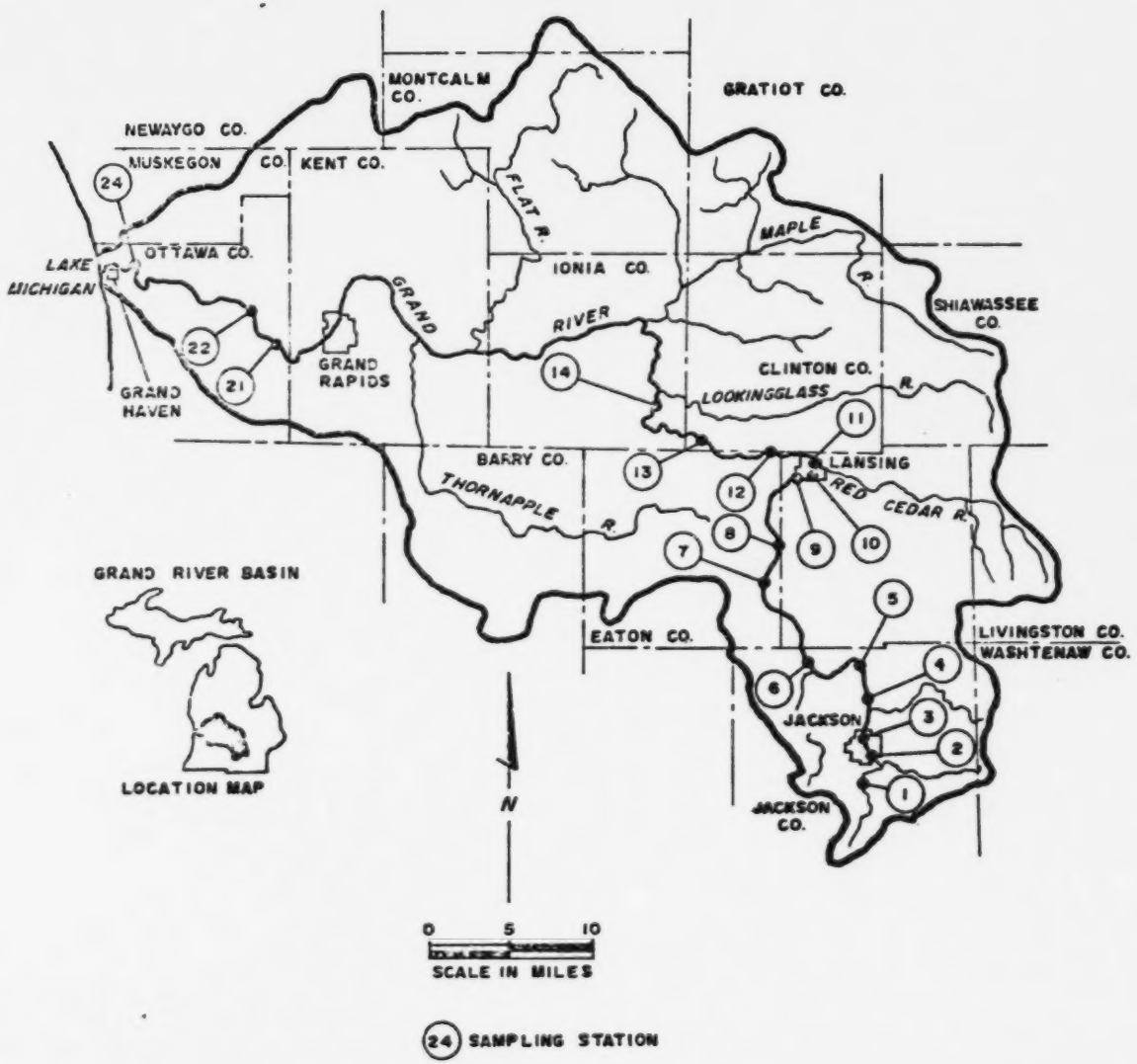


FIGURE 19. FISH COLLECTION LOCATIONS IN THE KALAMAZOO RIVER BASIN FOR HEAVY METALS ANALYSIS.

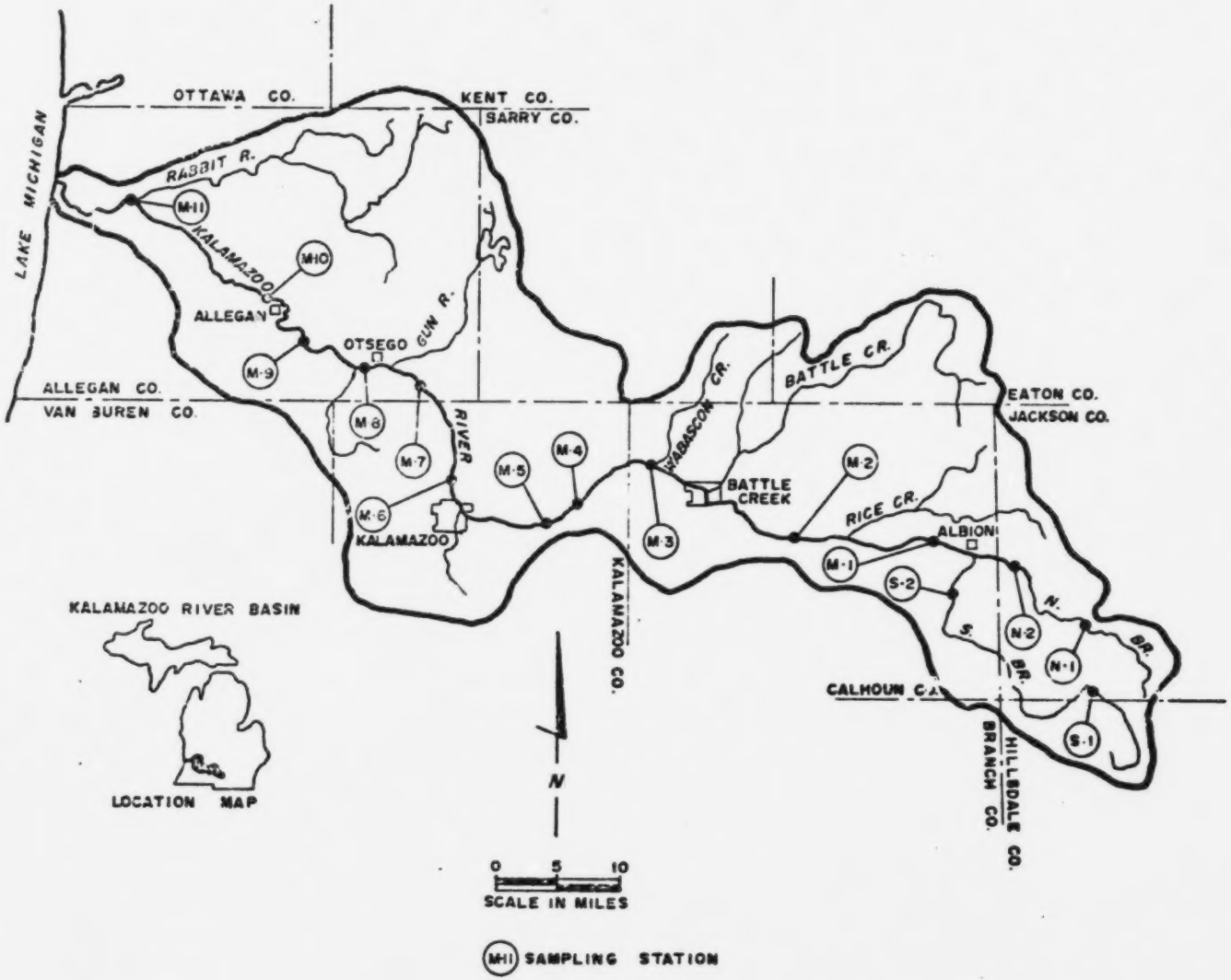


TABLE 1. CONSUMPTION OF METALS IN THE U.S.A.
IN 1,000's OF POUNDS (USDI, 1969)

Metal	Consumption
Arsenic	51,334
Cadmium	13,328
Chromium	2,632
Copper	4,194,000
Mercury	5,732
Lead	2,657,580
Zinc	2,667,398
Nickel	318,612
Beryllium	17,438
Selenium	1,216

TABLE 2. COMMON USES OF METALS

METAL	USED IN
Antimony	Alloys, metallurgical processes
Arsenic	In metallurgy to increase hardening and heat resistance, glassware, ceramics, tanneries, dyes, pesticides, and wood preservatives
Barium	Alloys, paints
Cadmium	Alloyed with copper, lead, silver, aluminum, nickel; electroplating; ceramics; pigments; photography; nuclear reactors
Cerium	Textile dyes, printing, arc lamps and neon tubes
Chromium	Metal plating, leather tanning, paints, dyes, explosives, ceramics, photography
Copper	Alloys, electrical equipment, pipes and roofing, textile processes, pigmentation tanning, photography, electroplating, insecticides and fungicides
Lead	Pipes, water storage chambers, dyes, paints
Magnesium	Light alloys, electrical and optical apparatus
Manganese	Steel alloys, dry-cell batteries, glass and ceramics, paints and varnishes, inks, dyes in matches, in fertilizers
Mercury	Dentistry, in scientific and electrical equipment, in chlor-alkali plants, medical products, detonators, pigments, photoengraving
Molybdenum	Metallurgy, electrical and electronic equipment, in glass and ceramic industry, and as part of the fertilizer for legumes
Nickel	Metal plating
Palladium	Photography, toning solutions, galvanocoatings
Selenium	Pigmentation in paints, dyes, and glass; in rectifiers, semiconductors, photoelectric cells, and in other electrical apparatus
Silver	Jewelry, silverware, alloys, electroplating, food processing, photography
Strontium	Polytechnic, signal lights, flares, matches
Thallium	Rat poison, dyes, pigments, in optical glass, depilatory
Thorium	Incandescent mantles and filaments for lamps
Tin	Mordants for reviving colors, fabric dyes, fingernail polish, lacquers, varnishes, fungicides, insecticides and antihelminthics
Vanadium	In metallurgy to increase hardness and malleability of steel, glass manufacture, photography, dye mordant
Zinc	Galvanizing pipes, alloys, electrical purposes, printing plates, dye-manufacturing, pharmaceuticals

McKee, J. E., and Harold W. Wolf. 1963. Water Quality Criteria, Second Edition. Publication 3-A April 1971. The Resources Agency of California.

TABLE 3. TRIBUTARIES TO LAKE MICHIGAN SHOWING METALS WHICH MIGHT BE FOUND AT HIGHER THAN BACKGROUND LEVELS DUE TO INDUSTRIES LOCATED THERE

MICHIGAN

Escanaba River - Zinc
Manistique River - Zinc
Bear River (Petosky) - Chromium, Copper, Nickel
Elk River - Chromium, Copper, Zinc
Boardman River - Chromium, Copper, Zinc
Manistee River - Nickel, Zinc
Pere Marquette River - Chromium, Copper, Nickel, Zinc
White River - Chromium, Copper, Nickel, Zinc
Muskegon River - Cadmium, Chromium, Copper, Nickel, Zinc
Mona Lake Outlet - Cadmium, Chromium, Copper, Nickel, Zinc
Grand River - Cadmium, Chromium, Copper Nickel, Zinc
Black River (Holland) - Cadmium, Chromium, Copper, Nickel, Zinc
Kalamazoo River - Cadmium, Chromium, Copper, Nickel, Zinc
Black River (South Haven) - Cadmium, Chromium, Copper, Nickel, Zinc
St. Joseph River - Cadmium, Chromium, Copper, Nickel, Zinc

INDIANA

The Calumet Area - Most
St. Joseph River - see Michigan

ILLINOIS

North Shore Sanitary District - Iron, Manganese, Zinc
U.S. Steel - Waukegan - Most

WISCONSIN

Milwaukee R. - Menominee River - Most but especially Cadmium, Chromium, Iron, Lead, Manganese, Zinc
Root River Basin - Racine - Unknown
Menominee River Basin - Arsenic, Copper, Zinc
Milwaukee STP - Most
Twin River - Unknown
Manitowoc - Possibly Cadmium, Chromium, Copper, Nickel, Zinc
Fox - Chromium, Copper, Iron, Nickel

TABLE 4.

Calculated particulate emission of trace elements from air pollution sources in Chicago, Milwaukee, and Northwest Indiana considered in this study

Element	Calculated source emission, short tons per year						Total short tons per year	Total kilograms per year ($\times 10^3$)
	Coal	Coke	Fuel Oil	Iron and steel	Cement	Transportation		
Ag			3				3	3
Al	40000	2800	955	4950	1000		50000	45000
As	46	3					49	44
B			4				4	4
Ba	176	12	45				230	210
Be	5	1					6	5
Br						800	800	725
Ca	10600	760	74	11600	17600		41000	37000
Cd	12	1					13	12
Cl						700	700	635
Co	25	2	28				55	50
Cr	80	6	22				110	100
Cu	109	8	28	3400			3500	3200
Fe	19500	1400	450	73000	930		95000	86000
K			16				16	15
Mg	2090	150	56	3360	500		6100	5500
Mn	67	5	6	5000			5100	4600
Mo	45	3	3.4				51	46
Na	1120	80	274				1500	1400
Ni	109	8	1030				1100	1000
P				170			170	150
Pb	328	24	33			2000	2400	2200
*S	550000	40000	150000	1000		7000	750000	680000
Se	5.5	0.4	15			1	22	20
Si	55800	4000	433	850	4000		65000	59000
Sn	13	1					14	13
Sr			6				6	5
Ti	2390	170	6				2600	2400
V	209	15	450				670	610
Zn	247	18	9	4000			4300	3900

* Total S (gaseous and particulate) included in order to calculate Se.

TABLE 5. COMPARISON OF AIR POLLUTION INVENTORY WITH RIVER INFLOW OF TRACE ELEMENTS TO LAKE MICHIGAN, METRIC UNITS.

	Cu	Ni	Zn
Air Pollution Emissions Inventory, Ton yr^{-1}	3200	1000	3900
Lake Michigan Rivers Approx. Mean Conc., 1963-1964, $\mu g l^{-1}$	90	40	30
Inflow to Lake Michigan Ton yr^{-1}*	2700	760	~500

*Estimated for total Lake Michigan drainage basin from contents and flow rates of individual rivers.

TABLE 6. YEARS REQUIRED TO RAISE LAKE MICHIGAN WATER CONCENTRATIONS 0.1 $\mu g l^{-1}$ FROM FALLOUT OF CHICAGO AREA AIR POLLUTION WITH 10% EFFICIENCY.

ELEMENT	YEARS
Cd	500
Cr	55
Cu	1.6
Fe	0.06
Mn	1.1
Ni	5.5
Pb	2.4
Se	73
Ti	2.5
V	9
Zn	1.3

TABLE 7. CONCENTRATIONS OF METALS IN LAKE MICHIGAN, 1962-1963
(FWPCA, 1968)

METAL	DEEPWATER		
	No. of Samples	Average (mg/l)	Range (mg/l)
Copper	58	<0.005*	
	3	0.010	0.007-0.012
Cadmium	61	<0.005	
Chromium	57	<0.005	
	3	.006	0.005-0.008
Nickel	33	<0.005	
	28	0.005	0.005-0.007
Zinc	48	<0.005	
	13	0.013	0.008-0.020

* 0.005 mg/l limit of detection when using 1000 ml sample.

TABLE 8.

AVERAGE TRACE ELEMENT CONCENTRATIONS
IN LAKE MICHIGAN CONSTITUENTS
ppm wet weight

ELEMENT	WATER	<200μ SEDIMENT CRUISE II	BULK SED. CRUISE I
Ag	.0003	.6	.6
Al	.027	40900	43700
As	.001	11	7
Au	.000002	.08	.10
Ba	.037	402	443
Br	.05	N.D.	N.D.
Ca	35	49400	18800
Ce	.0007	N.D.	N.D.
Cl	11	N.D.	N.D.
Co	.00018	8.8	5.7
Cr	.0017	55.9	58
Cs	.000014	2	1.2
Cu	∓.005	N.D.	17[1]
Eu	.0000086	.74	.47
Fe	.019	20100	13000
Hf	.000004	.095	3.5
Hg	.000027	.9	.6
I	.001	N.D.	N.D.
K	1.6	25600	12000
La	.0002	30	25
Lu	<.000009	.41	.19
Mg	11.5	22100	10800
Mn	.001	983	314
Mo	.002[1]	N.D.	N.D.
Na	5.0	8300	3660
Rb	.001	73	47
Sb	.00023	1	.51
Sc	.000003	6.6	3.7
Se	.000083	.6	.48
Sm	.00003	3.7	1.5
Sr	.097	122	101
Th	.0000024	7.0	3.7
V	.0002	47	20
Yb	<.000009	3.5	N.D.
Zn	.016	34[2]	12[2]

[1]Values obtained by Atomic Absorption.

[2]Values are probably too low due to scandium interference during analysis.

Table 8. (cont. for Zooplankton, Benthos and Phytoplankton)

ELEMENT	ZOOPLANKTON	BENTHOS	PHYTOPLANKTON
Ag	.04	.10	.09
Al	99	83	419
As	1	2	1.5
Au	.002	.003	.004
Ba	4	6	6
Br	88	36	8
Ca	1750[1]	2320	2000[1]
Ce	.2	.39	<.5
Cl	1440	1972	118
Co	.05	.06	.083
Cr	.35	.65	.43
Cs	.007	.033	.062
Cu	5	7	6
Eu	.002	.0017	.002
Fe	40	35	55
Hf	.005	.006	.005
Hg	.09	.14	.16
I	.91	.50	.80
K	970[1]	870[1]	725[1]
La	.066	.073	.22
Lu	.01	.01	<.02
Mg	240[1]	500	316[1]
Mn	3.7	3.7	11
Mo	5.9	3.9	.7
Na	265[1]	540[1]	310[1]
Rb	1.8	2.2	1.1
Sb	.08	.017	.07
Sc	.01	.011	N.D.
Se	.60	.48	.19
Sm	.015	.08	<.1
Sr	11	7.5	14
Th	.007	.007	<.02
V	.08	.065	.38
Yb	<.2	<.2	<.2
Zn	23	14	27

Table 9. Lake Michigan tributary concentrations, 6 February 1971.

RIVER	COND#	CA*	MG*	NA*	K*	FE†	MN†	CU†	NI†	CR†	MO†	ZN†	SR†
ST. JOSEPH	605.0	82.5	26.4	14.5	2.3	§							145.2
BLACK	466.0	52.3	19.2	18.8	2.5								205.4
KALAMAZOO	619.0	85.6	29.7	26.2	3.0	102.2	76.6	2.7	28.7	2.1	9.1	8.8	196.4
L. MACATAWA	289.0	40.4	11.6	9.6	3.2	145.7	44.1	1.8	8.1	2.6	3.8	7.1	178.3
PIGEON	320.0	44.1	10.0	5.5	3.0	143.5	64.8	0.3	8.8	2.8	36.8	5.5	130.2
GRAND	729.0	90.6	30.3	26.2	3.2	50.3	49.0	26.5	77.6	25.2	9.6	32.4	386.1
BLACK CREEK	476.0	47.3	12.6	33.6	2.5	308.9	129.6	1.5	9.2	2.6	0.7	8.8	123.2
MUSKEGON	405.0	50.4	16.6	13.2	1.9	81.4	28.2	3.2	9.2	9.6	9.6	8.8	166.7
WHITE RIVER	390.0	45.4	17.9	10.7	1.4	99.0	25.9	1.3	7.8	2.3	4.9	12.0	187.0
PENTWATER	429.0	51.7	23.1	9.2	1.7								166.7
PERE MARQUET	443.0	54.8	19.8	9.3	1.6	60.4	17.6	1.4	7.4	0.1	4.0	4.9	317.4
LINCOLN	338.0	42.2	14.8	8.5	1.6	115.1	25.6	2.0	6.0	0.1	2.7	4.9	114.5
BIG SABLE	338.0	35.6	14.5	8.1	1.3	27.2	8.7	1.6	5.3	0.1	2.2	1.7	166.7
MANISTEE	615.0	65.8	13.9	20.6	2.5	53.4	14.7	2.2	9.6	1.6	7.7	1.3	637.5
BETSIE	347.0	38.2	14.5	4.2	1.1	46.4	6.9	1.9	5.5	0.7	3.2	0.9	119.1
PLATTE	341.0	36.9	11.9	3.7	1.0	12.2	1.3	2.0	6.1	0.3	5.1	6.0	120.3
BOARDMAN	360.0	34.3	11.2	4.9	1.3	31.4	10.7	1.8	5.5	0.8	1.4	2.3	84.8
MANISTIQUE	210.0	25.7	7.2	1.4	0.8	180.7	21.0	2.4	2.8	0.4	0.1	6.0	87.7
WHITEFISH	299.0	39.6	17.8	1.7	1.0	143.5	8.2	0.9	4.8	0.3	2.9	5.5	56.0
ESCANABA	250.0	25.7	9.9	5.4	1.6	152.2	24.5	2.1	4.8	0.3	2.2	21.6	64.6
FORD RIVER	360.0	45.1	23.1	1.2	0.9	97.6	7.0	1.5	5.5	0.3	2.7	3.9	64.6
CEDAR	388.0	56.7	20.9	1.6	1.1	147.1	13.1	1.3	8.2	0.8	3.4	3.4	79.0
MENOMINEE	242.0	27.2	14.5	2.0	1.5	142.8	10.8	1.1	5.5		2.8	2.4	44.5
PESHTIGO	320.0	35.0	16.5	3.9	1.6	160.2	28.2	0.9	5.5	1.0	4.9	15.3	104.9
OCONTO	343.0	36.5	16.5	2.7	1.6	259.3	36.8	2.1	5.7	1.6	2.8	0.5	49.3
PENSAUKEE	560.0	59.8	29.7	5.6	2.3	89.7	14.7	2.3	12.9	1.2	5.4	2.0	116.9
FOX RIVER	446.0	42.1	23.8	14.0	2.9	38.9	17.5	2.7	9.1	7.5	7.1	7.5	167.6
TWO RIVERS	332.0	38.6	15.2	8.1	1.8	8.6	2.1	1.4	6.5	1.1	4.5	1.5	162.0
MANITOWOC	494.0	45.6	24.4	13.6	2.9	30.6	30.5	2.9	12.9	0.9	8.1	4.2	249.2
SHEBOYGAN	440.0	38.6	21.1	13.7	2.2	30.6	8.1	2.7	14.2	1.4	6.1	27.6	164.8
MILWAUKEE	797.0	36.9	20.5	74.3	4.7	15.3	24.5	4.4	19.7	5.1	9.2	32.2	531.3
ROOT RIVER	437.0	35.2	16.5	15.9	2.1	16.9	7.1	2.4	8.3	1.2	6.0	7.1	246.4

#μmho/cm.
*ppm.
†ppb.
§Element not determined.

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TABLE 10. Lake Michigan tributary concentrations, 25 May 1971.

RIVER	COND#	CA*	MG*	NA*	K*	FE†	MN†	CU†	NI†	CR†	MO†	ZN†	SR†	BA†
ST. JOSEPH	504.0	66.5	27.7	10.6	3.7	31.0	3.9	2.7	35.2	3.1	13.5	5.8	115.0	24.5
BLACK	459.0	53.1	29.3	27.9	2.6	41.5	42.1	3.6	13.0	2.1	8.2	11.0	127.0	26.0
KALAMAZOO	586.0	74.5	26.5	20.4	2.6	21.2	3.3	2.4	16.5	2.2	10.8	5.3	115.0	33.5
L. MACATAWA	620.0	50.6	16.9	50.4	§	25.1	35.4	3.6	14.4	1.7	13.1	6.1	124.0	36.5
PIGEON	303.0	44.5	12.2	4.5	2.8	92.2	30.8	2.4	9.2	1.6	35.8	7.4	98.6	14.0
GRAND	685.0	83.7	30.5	27.7	3.5	40.7	11.4	7.2	36.4	6.1	11.0	6.0	190.0	24.0
BLACK CR.	458.0	49.4	13.5	31.3	3.0	261.9	6.0	1.6	10.8	1.6	7.1	5.0	93.1	18.5
MUSKEGON	300.0	39.0	11.9	9.4	2.1	36.7	1.7	2.5	9.7	2.2	6.7	3.6	97.5	10.0
WHITE	373.0	45.1	18.4	11.2	1.8	52.3	19.8	1.5	9.7	1.4	5.1	4.3	103.0	12.5
PENTWATER	340.0	45.1	17.4	6.7	1.7	14.0	1.7	1.5	8.3	1.3	6.1	6.4	102.0	10.7

#μmho/cm.
*ppm.
†ppb.
§Element not determined.

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TABLE 11.Lake Michigan tributary concentrations, 26 May 1971.

RIVER	COND#	CA*	MG*	NA*	K*	FE†	MN†	CU†	NI†	CR†	MO†	ZN†	SR†	BA†
ST. JOSEPH	465.0	69.0	27.9	10.3	2.4	40.2	5.0	5.3	16.1	2.6	13.1	16.0	114.0	20.6
BLACK	415.0	52.4	20.7	16.8	2.3	154.6	60.7	4.4	16.4	2.1	6.3	5.1	145.0	26.2
KALAMAZOO	550.0	74.4	27.2	21.3	3.2	31.2	11.1	2.5	14.9	2.1	11.8	4.7	124.0	28.5
L. MACATAWA	372.0	44.2	14.2	19.6	3.9	37.4	2.1	1.8	9.9	1.6	7.7	2.4	124.0	21.9
PIGEON	290.0	44.2	12.1	4.3	2.7	48.4	21.5	1.4	8.5	1.3	32.0	2.6	114.0	15.7
GRAND	690.0	81.9	28.4	26.7	3.3	30.2	12.6	4.7	36.6	5.8	12.1	8.9	211.0	23.1
BLACK CR.	435.0	51.8	14.6	30.6	2.5	214.1	87.8	2.1	10.9	1.7	7.1	4.3	113.0	20.0
MUSKEGON	270.0	36.9	11.4	8.3	2.0	36.7	0.3	2.5	9.2	2.5	7.5	5.9	108.0	11.8
WHITE	330.0	44.2	17.6	9.0	1.8	95.3	12.3	1.7	9.5	1.4	§	3.3	145.0	11.1
PENTWATER	370.0	47.4	18.1	6.9	1.9	16.5	1.9	1.8	10.5	1.4	5.3	2.6	118.0	14.5
PERE MARQUET	400.0	56.2	19.5	11.2	2.5	37.4	2.5	2.1	10.9	2.8	6.3	6.7	197.0	17.2
LINCOLN	300.0	46.7	17.1	3.0	1.8	129.7	7.3	3.4	9.7	1.4	3.1	6.3	105.0	14.1
BIG SABLE	265.0	39.2	12.1	5.6	1.6	10.3	2.8	1.5	7.8	1.4	3.9	2.3	114.0	11.3

mho/cm.
* ppm.
ppb.
§ Element not determined.

TABLE 12. Lake Michigan tributary concentrations, 25 July 1971.

RIVER	COND#	CA*	MG*	NA*	K*	FE†	MN†	CU†	NI†	CR†	MO†	ZN†	SR†	BA†
TRAIL CR	697.0	46.0	16.3	39.5	1.1	23.6	91.2	52.3	22.8	331.0	11.3	3.9	68.0	11.7
TRAIL CR (Y)	738.0	24.0	15.5	71.4	6.4	16.4	89.4	139.0	584.0	25.4¶	13.5	6.5	108.2	14.3
GALIEN	532.0	65.6	26.3	7.8	2.2	51.0	56.5	2.1	7.0	1.9	3.0	2.6	84.1	47.7
ST.JOSEPH	450.0	61.7	21.6	12.6	2.1	14.1	3.7	4.5	8.4	0.9	6.7	2.9	87.7	33.6
BLACK R.	410.0	38.6	17.7	16.6	1.0	39.4	6.9	2.6	6.3	1.5	3.2	2.3	125.0	24.1
KALAMAZOO	565.0	82.7	21.6	25.0	2.6	37.9	6.2	3.5	12.8	1.4	4.5	2.6	124.0	33.8
MACATAWA	364.0	38.7	12.8	19.2	2.5	20.4	2.5	3.4	5.5	0.3	4.7	1.9	113.6	23.9
PIGEON	393.0	49.9	10.8	5.7	3.5	51.0	26.4	4.4	5.3	0.5	32.1	2.3	§	
GRAND	650.0	61.7	23.9	40.1	3.7	19.6	9.9	6.5	30.8	69.0	6.0	4.1	267.0	22.4
BLACK CR	677.0	53.9	12.5	46.9	1.9	218.0	46.5	1.3	6.5	1.8	4.9	2.2	91.6	15.4
MUSKEGON	335.0	38.7	12.8	12.6	1.5	13.1	2.3	4.1	5.6	2.4	5.0	2.3	117.0	10.1
WHITE	385.0	46.0	17.0	13.4	0.9	35.4	11.7	1.3	5.2	0.7	1.9	2.6	164.5	12.7
PENTWATER	337.0	31.3	16.8	8.6	1.4	10.9	2.3	2.8	4.0	1.8	2.8	1.9	118.5	9.0
PERE MARGUET	514.0	68.0	12.2	16.9	2.4	10.9	2.6	2.1	6.9	2.6	2.7	2.6	418.0	11.8
LINCOLN	318.0	38.6	15.8	3.7	1.1	35.1	9.2	2.1	3.9	1.0	1.5	1.9	82.8	7.4
BIG SABLE	298.0	31.3	12.1	6.4	1.1	9.9	2.3	5.7	4.8	0.3	2.1	2.3	106.0	11.0
MANISTEE	750.0	112.0	14.0	43.6	3.4	31.9	3.7	2.5	7.6	1.7	4.7	2.6	601.0	8.9

#μmho/cm
* ppm.
† ppb.
¶ x 10^3
§ Element not determined

TABLE 13. Lake Michigan tributary concentrations, 21 September 1971.

RIVER	COND#	CA*	MG*	NA*	K*	FE†	MN†	CU†	NI†	CR†	MO†	ZN†	SR†	BA†
TRAIL CR	356.0	36.3	15.0	9.7	2.1	27.3	16.3	3.4	8.3	1.7	5.8	2.5	97.1	20.5
CALIEN	574.0	70.9	26.3	11.3	2.8	23.9	33.9	3.0	8.3	1.5	3.5	2.5	60.2	42.4
ST JOSEPH	506.0	55.6	21.6	15.3	2.5	12.3	8.0	4.5	10.5	1.7	5.4	2.8	62.4	35.9
BLACK R	346.0	42.1	14.8	9.3	1.9	29.1	15.7	2.3	5.6	2.4	2.9	2.2	120.0	24.2
KALAMAZOO	594.0	59.4	21.6	30.0	3.0	40.5	56.6	3.0	12.0	2.7	5.0	2.8	111.0	37.8
MACATAWA	420.0	22.5	13.5	29.2	3.0	35.1	1.6	1.6	3.6	0.6	3.8	1.9	75.6	22.6
PIGEON	309.0	38.2	9.7	4.0	2.7	113.1	33.9	1.3	4.5	0.9	17.8	1.5	94.6	17.8
GRAND	679.0	65.6	21.6	39.6	3.8	28.3	6.0	7.2	23.6	5.9	6.3	2.5	279.0	28.0
BLACK CR	682.0	57.8	12.5	53.4	2.1	76.8	109.0	2.0	1.9	1.3	3.1	2.2	71.7	6.3
MUSKEGON	369.0	42.1	14.5	13.1	1.5	17.7	3.1	3.2	6.4	5.8	6.5	2.2	126.0	9.1
WHITE	529.0	36.3	15.0	41.9	1.6		2.2	1.5	5.0	1.7	4.6	1.9	140.0	10.7
PERE MARQUET	389.0	§	17.1	11.2	0.9	12.7	13.7	1.4	4.9	1.0	2.8	2.2	150.4	11.5
LINCOLN	348.0	44.0	17.1	4.0	1.8	6.4	8.0	1.2	0.5	1.4	2.3	1.9	71.7	14.1
BIG SABLE	285.0	34.3	13.0	7.2	0.9	8.1	2.0	1.6	4.7	0.7	2.3	1.9	113.0	8.3
MANISTEE	776.0	63.3	16.3	45.2	3.2	31.1	4.3	2.5	8.0	2.9	5.4	2.8	510.0	13.1
BETSIE	318.0	40.1	13.8	4.2	1.1	28.9	2.2	1.6	3.5	0.6	3.6	2.2	90.6	12.3
PLATTE	303.0	40.1	13.3	3.0	0.8		1.9	1.5	4.3	0.6	2.2	2.2	76.2	9.8
BOARDMAN	343.0	51.7	12.8	4.0	1.2	9.4	6.6	2.0	0.1	1.0	2.3	2.2	37.3	9.7

#umho/cm.
* ppm.
† ppb.
§ Element not determined.

TABLE 14. Mean concentration and coefficient of variation.

RIVER	COND[#]	CA[*]	MG[*]	NA[*]	K[*]	FE[†]	MN[†]	CU[†]	NI[†]	CR[†]	MO[†]	ZN[†]	SR[†]	BA[†]
ST.JOSEPH	506.0	67.1	25.0	12.7	2.6	24.4	5.1	4.2	17.5	2.1	9.5	6.9	104.9	28.6
	0.1	0.1	0.1	0.2	0.2	0.5	0.3	0.2	0.6	0.4	0.4	0.8	0.3	0.2
BLACK	420.2	46.5	20.2	18.1	2.0	36.7	21.6	2.8	8.3	2.0	4.8	5.2	144.3	24.8
	0.1	0.1	0.3	0.4	0.3	0.1	0.7	0.2	0.4	0.2	0.5	0.8	0.2	0.0
KALAMAZOO	582.8	75.3	25.3	24.7	2.9	46.6	30.8	2.8	17.0	2.1	8.2	4.8	134.1	33.4
	0.0	0.1	0.1	0.2	0.1	0.6	1.0	0.1	0.4	0.2	0.4	0.5	0.2	0.1
L.MACATAWA	413.0	39.3	13.8	25.6	3.1	52.7	17.1	2.4	8.3	1.4	6.6	3.9	123.1	34.1
	0.3	0.2	0.1	0.5	0.2	0.9	1.1	0.4	0.4	0.6	0.5	0.6	0.3	0.5
PIGEON	323.0	44.2	11.0	4.8	2.9	89.6	35.5	2.0	7.3	1.4	30.9	3.9	109.3	15.8
	0.1	0.1	0.1	0.1	0.1	0.4	0.4	0.7	0.3	0.5	0.2	0.6	0.1	0.1
GRAND	686.6	76.7	26.9	32.1	3.5	33.8	17.8	10.4	41.0	22.4	9.0	10.8	266.6	24.4
	0.0	0.1	0.1	0.2	0.1	0.3	0.9	0.8	0.5	1.1	0.3	1.0	0.3	0.1
MUSKEGON	335.8	41.4	13.4	11.3	1.8	37.1	7.1	3.1	8.0	4.5	7.1	4.6	123.0	10.2
	0.1	0.1	0.1	0.2	0.1	0.7	1.5	0.2	0.2	0.6	0.2	0.5	0.2	0.1
WHITE RIVER	401.4	43.4	17.2	17.2	1.5	56.5	14.4	1.5	7.4	1.5	4.1	4.8	147.9	11.7
	0.2	0.1	0.1	0.7	0.2	0.7	0.6	0.1	0.3	0.3	0.3	0.8	0.2	0.1
PENTWATER	356.5	43.9	18.8	7.8	1.7	13.8	2.0	2.0	7.6	1.5	4.7	3.6	126.3	11.4
	0.1	0.2	0.1	0.1	0.1	0.2	0.1	0.3	0.4	0.1	0.3	0.5	0.2	0.2
PERE MARQU	436.5	59.7	17.1	12.1	1.9	30.3	9.1	1.7	7.5	1.6	3.9	4.1	270.7	13.5
	0.1	0.1	0.2	0.2	0.3	0.7	0.7	0.2	0.3	0.7	0.4	0.4	0.4	0.2
LINCOLN	326.0	42.9	16.2	3.5	1.6	71.6	12.5	2.2	5.0	1.0	2.4	3.7	93.5	11.9
	0.1	0.1	0.1	0.1	0.2	0.7	0.6	0.4	0.7	0.5	0.2	0.5	0.2	0.3
BIG SABLE	296.5	35.1	12.9	6.8	1.2	13.9	3.9	2.6	5.6	0.6	2.6	2.0	124.9	10.2
	0.1	0.1	0.1	0.1	0.2	0.6	0.7	0.7	0.2	0.8	0.3	0.1	0.2	0.1
MANISTEE	713.7	80.4	14.7	36.5	3.0	38.8	7.6	2.4	8.4	2.1	5.9	2.2	582.8	10.7
	0.1	0.3	0.1	0.3	0.1	0.3	0.7	0.1	0.1	0.3	0.2	0.3	0.1	0.2
PLATTE	322.0	38.5	12.6	3.3	0.9	12.2	1.6	1.7	5.2	0.4	3.6	4.1	98.2	9.8
	0.1	0.0	0.1	0.1	0.1	0.0	0.2	0.1	0.2	0.3	0.4	0.5	0.2	0.0
BETSIE	332.5	39.1	14.1	4.2	1.1	37.6	4.5	1.7	4.5	0.6	3.4	1.5	104.8	12.3
	0.0	0.0	0.0	0.0	0.0	0.2	0.5	0.1	0.2	0.1	0.1	0.4	0.1	0.0
BOARDMAN	351.5	43.0	12.0	4.4	1.2	20.4	8.6	1.9	2.8	0.9	1.8	2.2	61.0	9.7
	0.0	0.2	0.1	0.1	0.0	0.5	0.2	0.1	1.0	0.1	0.2	0.0	0.4	0.0

[#] umho/cm.
[*] ppm.
[†] ppb.

TABLE 15. Daily loadings of chromium in selected rivers tributary to Lake Michigan.

RIVER	Gauged# drainage area	Total# drainage area	Ratio	Flow at mouth (CFS)*					Daily loading (kg/day)				
				2/6†	5/25	5/26	7/25	9/21	2/6	5/25	5/26	7/25	9/21
ST. JOSEPH	3666	4680	1.27		2690	2882	1981	1714	—	20.3	18.2	4.1	7.1
BLACK (SOUTH HAVEN)	83.6	287	3.43		137	141	154	250	—	0.7	0.7	0.6	1.5
KALAMAZOO	1600	1980	1.24	1785	1265	1661	1500	1252	9.1	6.7	8.4	5.1	8.2
L MACATAWA	65.8	145	2.20	374	22	22	53	10	2.4	0.1	0.1	—	0.0
GRAND	4900	5534	1.13	3322	2622	2814	1153	1435	202	38.7	39.5	192.3	20.5
MUSKEGON	2350	2663	1.13	2260	2192	2893	1187	1055	53	11.7	17.5	6.9	14.9
WHITE	380	510	1.34	496	594	705	287	291	2.8	2.0	2.4	0.5	1.2
PERE MARQUETTE	709	770	1.09	632		876	472	406	0.2	—§	5.9	3.0	1.0
BIG SABLE	127	194	1.53	199		257	154	132	0.0	—	0.9	0.1	0.2
MANISTEE	1780	2000	1.12	2464			1355	1736	9.6	—	—	5.6	12.2

Sq. miles.
*U.S. Dept. Int. 1972 (winter flows may be inaccurate due to ice covers). Flows not entered where concentrations were not determined.
†Month/day.
§Concentration not determined.

TABLE 16. Mean daily loading and standard deviation.

RIVER	CFS#	CA*	MG*	NA*	K*	FE†	MN†	CU†	NI†	CR†	MO†	ZN†	SR†	BA†
ST. JOSEPH	3398.0	551.3	205.8	104.1	21.4	200.6	42.3	34.9	144.3	17.0	78.5	56.5	862.0	235.5
		± 73.8	23.5	16.5	4.6	96.0	14.1	7.8	86.9	7.1	30.9	44.4	229.9	51.8
BLACK	200.0	22.5	9.8	8.8	1.0	17.7	10.4	1.4	4.0	1.0	2.3	2.5	69.8	12.0
		3.1	2.6	3.2	0.3	2.6	7.2	0.3	1.6	0.2	1.2	2.0	17.1	0.4
KALAMAZOO	1296.0	236.1	79.4	77.6	9.0	146.1	96.4	8.8	53.2	6.6	25.8	15.2	420.4	104.7
		28.6	10.1	11.7	0.8	89.6	94.2	1.2	19.0	1.3	9.3	7.0	99.0	10.3
L. MACATAWA	45.2	4.3	1.5	2.8	0.3	5.8	1.9	0.3	0.9	0.1	0.7	0.4	13.5	3.7
		1.0	0.2	1.5	0.1	5.1	2.0	0.1	0.4	0.1	0.4	0.2	3.6	1.8
GRAND	3362.0	623.8	219.1	260.8	28.5	275.1	144.6	84.7	333.5	182.2	73.2	87.7	2168.5	198.3
		90.4	29.1	51.9	1.9	86.4	128.2	65.8	153.8	199.0	20.0	89.6	556.2	17.6
MUSKEGON	1889.0	189.3	61.4	51.7	8.3	169.6	32.5	14.2	36.7	20.6	32.3	20.8	562.3	46.9
		21.9	8.7	9.4	1.1	110.3	48.4	2.7	7.7	13.1	6.9	11.4	108.7	4.5
WHITE RIVER	367.0	38.5	15.3	15.3	1.3	50.1	12.8	1.3	6.6	1.3	3.7	4.3	131.3	10.4
		3.2	1.0	11.0	0.3	33.1	7.1	0.1	1.8	0.4	1.2	3.3	24.8	0.6
PENTWATER	150.0	15.9	6.8	2.8	0.6	5.0	0.7	0.7	2.8	0.5	1.7	1.3	45.8	4.1
		2.8	0.9	0.4	0.1	0.8	0.1	0.2	1.0	0.1	0.5	0.7	8.8	0.8
PERE MARQU	608.0	87.4	25.2	17.9	2.8	44.6	13.4	2.6	11.1	2.4	5.8	6.0	398.2	19.9
		8.7	4.5	4.2	0.9	29.8	9.8	0.5	3.2	1.7	2.1	2.7	153.9	3.9
LINCOLN	70.0	7.3	2.7	0.6	0.3	12.1	2.1	0.4	0.9	0.2	0.4	0.6	15.8	2.0
		0.5	0.2	0.1	0.0	8.8	1.3	0.1	0.6	0.1	0.1	0.3	2.9	< 0.5
BIG SABLE	137.0	11.6	4.3	2.3	0.4	4.6	1.3	0.9	1.9	0.2	0.9	0.7	41.4	3.4
		0.9	0.3	0.3	0.1	2.6	0.9	0.6	0.4	0.2	0.2	0.1	8.1	0.4
MANISTEE	1933.0	375.8	68.7	170.5	14.2	181.4	35.4	11.2	39.3	9.7	27.7	10.4	2725.5	90.0
		104.7	9.3	52.6	1.8	48.3	23.6	0.7	4.0	2.8	6.0	3.1	250.7	11.2
BETSIE	175.0	16.6	6.0	1.8	0.5	15.9	1.9	0.7	1.9	0.3	1.4	0.7	44.4	5.2
		0.4	0.1	0.0	0.0	3.7	1.0	0.1	0.4	0.0	0.1	0.3	6.0	0.0
BOARDMAN	186.0	19.3	5.4	2.0	0.6	9.2	3.9	0.9	1.3	0.4	0.8	1.0	27.5	4.4
		3.9	0.4	0.2	0.0	4.9	0.9	0.0	1.2	0.0	0.2	0.0	10.7	0.0

Mean annual flow (cu ft/sec).
* 10^3 kg/day
†kg/day

TABLE 17. Mean daily tributary inputs of dissolved metals to Lake Michigan and particulate emissions into the atmosphere from air pollution sources in Chicago, Milwaukee, and northwest Indiana.*

Element	Tributary inputs (metric tons/day)	Atmospheric emissions
Ca	5800	100
Mg	1800	15
Na	1400	4
K	230	0.04
Fe	4.0	200
Mn	1.3	13
Cu	0.38	9
Ni	1.4	3
Cr	0.46	0.3
Mo	0.80	0.8
Zn	0.50	11
Sr	19	0.01
Ba	2.0	0.6

*Winchester and Nifong (1970).

TABLE 18. CONCENTRATIONS OF METALS IN WATER FROM TWO WISCONSIN TRIBUTARIES TO LAKE MICHIGAN

Tributary	Metal	# of Samples	Mean (µg/l)	Minimum	Maximum
Fox River					
	Cadmium	11	.01*		
	Chromium	11	.026	.02	.05
	Copper	11	.022	.01	.04
	Iron (total)	5	1.088	.44	4.00
	Lead	11	.189	.05	.45
	Manganese	4	.07	.04	.13
	Nickel	11	.054	.02	.20
	Zinc	1	.02		
Milwaukee River					
	Cadmium	8	.01*		
	Chromium	8	.025	.02	.03
	Copper	8	.02	.01	.03
	Iron (total)	1	.44	.	
	Lead	8	.046	.02	.05
	Manganese	1	.05		
	Nickel	8	.04*		

* All values < detectable.

TABLE 19. AVERAGE CONCENTRATIONS OF TRACE ELEMENTS, IRON OXIDE, ORGANIC CARBON, AND LESS THAN 2-MICRON CLAY IN SOUTHERN LAKE MICHIGAN CORES

Constituent	Top interval*	1 - 7 cm	4 - 12 cm*	8 - 20 cm	16 cm and deeper
Ba (ppm)	65 ± 38 (17)†	60 ± 29 (12)	47 ± 21 (18)	48 ± 24 (17)	35 — (19)
Cr (ppm)	70 ± 30 (22)	66 ± 22 (15)	57 ± 20 (21)	55 ± 16 (19)	52 — (24)
Cu (ppm)	41 ± 24 (22)	33 ± 14 (15)	28 ± 10 (21)	27 ± 9 (19)	20 ± 9 (24)
Pb (ppm)	79 ± 54 (22)	65 ± 45 (15)	44 ± 37 (21)	30 ± 18 (19)	20 ± 3 (23)
Zn (ppm)	179 ± 125 (22)	148 ± 107 (15)	115 ± 71 (21)	86 ± 38 (19)	66 ± 12 (23)
Ni (ppm)	34 ± 12 (22)	32 ± 8 (15)	34 ± 8 (21)	33 ± 11 (19)	35 ± 6 (23)
MnO (%)	0.065 ± 0.033 (22)	0.070 ± 0.022 (15)	0.057 ± 0.023 (21)	0.057 ± 0.023 (19)	0.050 ± 0.018 (24)
Fe_2O_3 (%)	3.99 ± 1.28 (22)	3.91 ± 1.02 (15)	3.81 ± 1.03 (21)	3.54 ± 1.17 (19)	3.35 ± 0.65 (24)
Organic carbon (%)	2.35 ± 1.44 (22)	2.13 ± 1.20 (15)	1.85 ± 0.95 (21)	1.88 ± 1.04 (19)	1.40 ± 0.48 (23)
< 2μ clay (%)	31.6 ± 19.3 (20)	29.7 ± 13.6 (14)	34.5 ± 10.8 (19)	34.3 ± 15.6 (18)	41.4 ± 8.8 (24)

* Values given for each interval are, in order, average trace element concentration, standard deviation, and number of samples used to compute the mean.

† Numbers enclosed in parentheses equal number of samples used in calculating the correlation coefficient.

From Shimp, et, al., Environmental Geology Notes, Number 41, January 1971, Illinois State Geological Survey

TABLE 20. HEAVY METAL CONCENTRATIONS IN SEDIMENT SAMPLES FROM 10 BACKGROUND WATER QUALITY STATIONS IN MICHIGAN'S PORTION OF THE LAKE MICHIGAN BASIN, OCTOBER 1970. (CONCENTRATIONS IN mg/kg, DRY WEIGHT).

Site No.	Station Name and Description	Date	Hg Total	As	Cd	Cr^{+6}	Co	Pb	Zn
39	S. Br. Kalamazoo R, Bridge, Sec. 11 Homer Township, Calhoun County.	10-12-70	0.19	0	6	3	52	58	24
41	Rocky River, Floating Bridge Road, Sec. 25, Flowerfield Township, St. Joseph County	10-12-70	0.14	1	1	2	6	11	17
42	Paw Paw R., 37.5 St. Bridge, Sec. 26, Waverly Township, VanBuren County	10-12-70	0.14	1	1	2	9	13	17
46	Crockery Cr., Leonard Street Bridge, Sec. 23, Crockery Twp., Ottawa Co.. . . .	10-15-70	0.13	0	1	2	9	26	24
49	E. Br. Galien R., Glendora Road Bridge, Sec. 8, Weesaw Township, Berrien Co.. . .	10-12-70	0.24	0	9	0	50	56	34
62	Pine River, Skoakum Road, Sec. 32, Dover Township, Lake County	10-15-70	0.22	0	7	2	62	65	20
65	Muskegon River, Pine Road, Sec. 34, Winterfield Township, Clair County. . . .	10-14-70	0.19	0	1	2	6	6	10
66	Betsie River, Thompsonville Road, Sec. 24, Weldon Twp., Benzie County . . .	10-14-70	0.19	0	0	1	4	2	4
69	Jordan R., Chestonia Road, Jordan Township, Antrim County	10-13-70	0.20	0	3	1	14	21	6
87	E. Br. Escanaba R., M-35 Bridge, Forsyth Township, Marquette Co.	10-14-70	0.20	0	1	0	7	15	34
	Mean		0.17	0.2	3.0	1.5	21.9	27.3	19.0
	Range		0.13-0.24	9-1.0	1-9	0-3	4-62	2-65	4-34

TABLE 21. HEAVY METAL CONCENTRATIONS IN SEDIMENT SAMPLES FROM THREE STREAM LOCATIONS BELOW MAJOR MUNICIPAL AND INDUSTRIAL COMPLEXES IN THE MICHIGAN PORTION OF THE LAKE MICHIGAN BASIN, OCTOBER 1970. (CONCENTRATIONS IN mg/kg, DRY WEIGHT).

Station Name	Date	Mercury (total) FWQA Method	As	Cd	Cr^6	Co	Pb	Zn
Kalamazoo River at Parchment.	10-22-70	2.4	0	5	1	19	200	310
Red Cedar River at Lansing.	10-23-70	2.4	0	8	1	54	320	330
Grand River at Grandville	10-22-70	0.6	0	7	0	34	350	230
Average.		1.8	0	6.7	0.7	35.7	290	290

TABLE 22. CONCENTRATIONS OF As, Sb, Cu, Zn, Au, Cd, Hg, AND Co IN SEDIMENT SAMPLES COLLECTED AT 35 INDUSTRIAL AND MUNICIPAL LOCATIONS IN THE MICHIGAN PORTION OF THE LAKE MICHIGAN BASIN, APRIL-MAY 1970. ANALYSES PERFORMED BY DOW CHEMICAL COMPANY WITH NEUTRON ACTIVATION. (ALL CONCENTRATIONS IN PARTS PER MILLION (ppm) EXCEPT Au WHICH IS IN PARTS PER BILLION; DRY WEIGHT)

Station Description	As	Sb	Cu	Zn	Au	Cd	Hg	Cr
General Electric, Edmore - open drain PRR tracks.	91.70	14.90	150.0	239	75.0	6.81	38.200	130.0
Grand River, 75' below Lansing WWTP	13.50	6.17	411.0	347	4.0	3.06	0.316	125.0
Grand River, 150' below Jackson WWTP outfall.	28.40	3.83	170.0	976	340.0	37.40	0.787	781.0
Cedar Lake.	2.48	0.41	4.8	198	0.9	<3.30	0.094	5.8
Pine River, St. Louis	7.35	0.47	2351.0	275	89.3	1.83	0.797	159.0
Rogue River, 10' below Rockford Paper outfall	24.10	1.46	149.0	111	61.1	0.81	2.120	35.3
Grand River, Grand Rapids, 500' from PCA outfall.	12.00	31.70	396.0	620	727.0	11.10	1.760	320.0
Grand River below Grand Rapids WWTP	9.05	4.72	214.0	591	271.0	5.91	0.984	192.0
Grand River, 50 yds. below Plaster Creek.	7.78	2.37	99.7	281	9.1	4.22	0.361	110.0
Ditch below Wyoming WWTP.	7.97	1.40	64.0	235	60.1	1.85	0.633	102.0
St. Joseph River near mouth	1.14	0.62	2.0	19	0.8	0.18	0.013	3.1
Paw Paw River, 75 yds. below Watervliet Paper Co.	5.41	0.17	36.2	107	133.0	0.38	2.640	15.4
Grand River below Grandville WWTP	5.33	1.26	73.6	215	52.9	5.40	0.418	178.0
Grand River at Grand Haven.	7.15	3.91	246.0	579	6.4	9.66	0.872	881.0
Black River below Holland WWTP.	13.00	0.67	70.4	283	162.0	4.13	0.672	97.5
Kalamazoo River below Saugatuck	17.00	0.54	68.7	327	30.0	4.12	0.290	25.2
Black River below South Haven	8.22	0.18	13.6	67	14.0	0.29	0.469	62.5
St. Joseph River below South Bend	6.24	0.62	36.6	131	14.5	2.22	0.194	32.3
Menominee River below Ansul Chemical Company.	15.80	3.31	12.4	54	9.5	0.78	0.593	3.6
Menominee River below American Can Company.	7.85	0.80	12.1	81	6.1	0.18	0.469	7.9
Manistee Lake, Michigan Chemical.	8.34	1.74	298.0	386	75.3	7.82	0.861	31.6
Manistee Lake, Standard Lime and Refractories	3.51	0.20	11.9	67	13.4	0.88	0.721	23.9
Pere Marquette River below Ludington WWTP	2.00	0.52	49.3	524	167.0	18.20	0.317	260.0
Pere Marquette below Dow Chemical	4.79	0.93	23.3	141	69.0	0.69	0.235	38.1
Little Black Creek near mouth	11.40	18.30	296.0	2066	54.8	23.40	0.354	334.0
Muskegon River, Continental Motors, US-31 Plant	3.90	0.26	34.3	73	25.3	1.26	1.240	15.1
Muskegon River, Ott Chemical outfall.	5.92	0.30	7.1	40	10.1	0.65	0.163	17.8
White Lake, Whitehall Leather	5.61	1.12	36.9	147	3.9	1.49	3.870	20390.0*
Muskegon Lake, Continental Motors, Getty Street Plant	6.41	0.50	83.3	267	11.8	7.14	0.401	50.7
Muskegon River, below Muskegon WWTP	7.79	1.40	29.0	211	22.3	2.51	0.260	83.8
Manistee River, Washington Street	11.50	0.75	124.0	182	40.7	3.95	0.412	64.1
Kalamazoo River, below Hercules, Inc.	25.30	4.72	247.0	742	11.4	8.46	2.660	329.0
Portage Creek, Allied Paper	24.60	1.58	161.0	428	54.9	2.45	2.380	60.2
Kalamazoo River, below Kalamazoo WWTP	8.23	2.42	230.0	447	16.3	7.20	2.110	226.0
Kalamazoo River, below Battle Creek WWTP.	21.40	2.19	480.0	1509	302.0	3.64	3.630	2664.0
Average.	12.37	3.24	186.5	364	82.2	5.81	2.020	782.5

*Minimum

TABLE 23. CONCENTRATIONS OF HEAVY METALS IN SEDIMENTS FROM KALAMAZOO RIVER, AUGUST 1971. (CONCENTRATIONS IN ppm; WET WEIGHT)

Stream	Location	County	Ni	Cu	Zn	Hg	Cd	As	Pb	Total
N. Br. Kalamazoo R.	Sears Road	Jackson	3.0	<1	60	<0.1	0.2	20	20	<10
S. Br. Kalamazoo R.	Webster Street, Homer	Calhoun	3.0	3	27	<0.1	0.2	2.7	16	<10
Kalamazoo R.	15-1/2 Mile Road	Calhoun	7.0	10	115	0.10	1.4	2.5	32	24
Battle Creek R.	Jackson St. (M-37) in Battle Creek	Calhoun	4.0	50	130	0.15	0.6	4.2	100	16
Kalamazoo R.	Stringham Road in Battle Creek	Calhoun	7.0	17	140	0.13	0.4	2.5	36	12
Kalamazoo R.	Ft. Custer Bridge, Left 1/3 (just below Wabasacon Creek)	Calhoun	20.0	33	155	0.14	0.6	3.0	40	48
Kalamazoo R.	Patterson Ave. in Kalamazoo	Kalamazoo	16.0	37	115	0.44	0.8	3.7	84	16
Kalamazoo R.	Mosel St. in Parchment	Kalamazoo	16.0	44	165	0.40	1.0	1.8	125	44
Kalamazoo R.	M-89 West of Otsego	Allegan	8.5	30	95	0.33	0.8	2.5	48	16
Kalamazoo R.	Old U.S.-31	Allegan	4.0	7	60	<0.1	0.4	0.8	20	<10

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TABLE 24.
MERCURY CONTENT OF SEDIMENTS AND WATER FROM THE UPPER FOX, SHEBOYGAN, MILWAUKEE AND FOX (ILLINOIS) RIVER AND PEWAUKEE, BIG GREEN AND GENEVA LAKES

*Sample No.	Miles	Location	Mercury Content (ppm) Sediment	Water
		Upper Fox River		
1	160.9	Above Portage STP	<0.05	------
2	160.7	Portage STP	----	0.006
3	160.3	Hwy. "33" Bridge-Average 3 samples	3.7	<0.0005
4	160	Above Portage Canal	6.8	<0.0005
5	159.6	In Portage Canal	0.2	<0.0005
6	159	Below Portage Canal	6.8	<0.0005
7	90.7	100 yds. below Berlin STP	<0.05	<0.0005
8	90.6	200 yds. below Berlin STP	<0.05	<0.0005
9	76.1	Hwy. "21" Bridge -Omro	----	0.003
	69.9	Wolf River	----	------
10	49	Lake Winnebago - North End	0.25	------
	0	Green Bay		
		Sheboygan River		
11	1.5	8th St. Bridge - Sheboygan	----	<0.00005
	0	Lake Michigan		
		Milwaukee River		
12	51.8	Hwy. "MY" Bridge below West Bend	0.35	<0.00005
13	18.8	Above Thiensville Dam	0.20	<0.00005
14	3.1	Above North Avenue Dam	0.60	<0.00005
	0	Inner Milwaukee Harbor		
15		(a) Milwaukee River-Interstate Bridge	0.85	<0.00005
16		(b) Menominee River-Union Station	0.30	<0.00005
17		(c) Kinnickinnic River-Kinnickinnic Bridge	0.30	<0.00005
18		(d) Turning Basin	1.70	<0.00005
	0	Outer Milwaukee Harbor		
19		(a) 500 ft. East of Jones Island	3.8	<0.00005
20		(b) 300 ft. North of South Shore Harbor	----	<0.00005
21		(c) 500 ft. East of McKinley Beach	----	<0.00005
		Fox (Illinois) River		
22	56.5	Hwy. "D" Bridge Below Waukesha	0.75	<0.00005
23	11.8	Hwy. "JB" Bridge below Burlington	<0.05	<0.00005
	0	Illinois State Line		
		Lakes		
24		Pewaukee	<0.05	<0.00005
25		Big Green (1)	0.20	-------
		(2)	<0.05	-------
26		Geneva	0.1	<0.00005

*Sample numbers correspond to sample locations on Figure 5 (Konrad, 1971)

* TABLE 25. SELECTED TRACE ELEMENT CONCENTRATIONS IN BIOTA OF LAKE MICHIGAN

Element	Phytoplankton (ppm-dry tissue)*		Zooplankton (ppm-dry tissue)*		Benthos (ppm-dry tissue)*		Fishes (ppb-dry tissue)†
Arsenic				(3,500)			3 - 43 ± 12
Barium		(937)		(473)	20.3 ± 1.7	(985)	<200
Bromine		(4,730)		(6,630)		(5,000)	
Cadmium							62 ± 15 - 76 ± 8
Chromium	2.36 ± 1.18		5.88 ± 2.61		2.51 ± 1.26		900 ± 500 - 1600 ± 200
Cobalt		(207)		(123)		(109)	24 ± 2 - 42 ± 15
Copper	28.1 ± 1.5	(14,500)	28.8 ± 0.4	(14,800)	24.0 ± 1.5	(12,400)	800 ± 150 - 2700 ± 600
Iron	166 ± 6	(36,000)	110 ± 5	(26,800)	112 ± 7	(20,100)	
Manganese	10.6 ± 0.6	(14,100)	17.0 ± 0.4	(11,900)	13.7 ± 0.6	(31,000)	
Mercury	1 - 14††	(>10,000)	1 - 14††	(>10,000)	1 - 6††	(>10,000)	130
Selenium	0.5 - 6††		0.5 - 6††		1 - 4††		
Strontium	15.1 ± 1.4				49.5 ± 1.3		
Zinc	88.4 ± 5.9	(2,710)	104 ± 3	(3,550)	66.9 ± 6.1	(3,670)	

*Trace element concentrations in phytoplankton, zooplankton, and benthos from Ayers (1970). Values in parentheses are enrichment factors computed against the concentration of the element in Lake Michigan water. The samples were lightly contaminated with sediment.

†Trace element concentrations in whole fish are from Lucas, Edgington, and Colby (1970), except for the value for mercury, which is an average for fishes of Lake Michigan (Edgington, unpublished data, 1971).

††Data for mercury and selenium are from Copeland (1970).

*Source: Leland, H. V. and N. F. Shimp, 1971. Trace elements in Southern L. Michigan. Preprint to be published in "Chemistry and Biology of Trace Elements in the Enfironment". University of Illinois Press; p. 25.

TABLE 26. CONCENTRATION OF LEAD, MERCURY AND SELENIUM FOUND IN FLESH OF NINE SPECIES OF LAKE MICHIGAN FISH. VALUES EXPRESSED AS PARTS PER MILLION ON A WET WEIGHT BASIS.

LOCATION	SPECIES	NUMBER OF FISH IN SAMPLE	PARTS PER MILLION		
			LEAD	MERCURY	SELENIUM*
WAUKEGAN					
	Smelt	3	0.347	0.227	0.652
	Alewife	4	0.135	0.271	0.095
	Chub	15	0.077	0.212	0.325
NORTH CHICAGO					
	Coho Salmon	11	0.063	0.329	0.317**
	Brown Trout	3	0.292***	0.302	0.236
	Carp	1	-----	0.294	0.148
	Goldfish	4	0.410	0.654	0.220
	Carp X Goldfish	1	0.005	0.266	0.476
	White Sucker	1	-----	0.290	0.550
CHICAGO					
	Yellow Perch	2	0.207	0.273	0.480
	Coho Salmon	3	0.560	0.498	0.183
	Carp	2	0.075	0.076	0.294
	Average for all fish		0.165	0.303	0.311

* Values reported on samples that were somewhat dehydrated from storage.
** Value on ten fish
*** Value based on one fish
Source: Ill. Env. Prot. Agency. 1970. Lake Michigan Open Water and Lake Bed Report, p. 63.

TABLE 27. CONCENTRATIONS OF METALS FOUND IN EDIBLE PORTION OF FISH FROM THE GRAND RIVER, JACKSON TO GRAND HAVEN, MICHIGAN, JULY 1970

STATION	STATION LOCATIONS	SPECIES	METALS (ppm)					
			Cu	Ni	Zn	Cr	Cd	Hg
1	Reed & Jefferson Rds., above Jackson at US-127	Carp	0.3	<0.4	8.0	<0.05	<0.05	----
		Bass	0.2	<0.4	11.0	<0.05	<0.05	----
		Bullhead	0.2	<0.4	9.0	<0.05	<0.05	----
2	High St., above Jackson	Carp	0.4	<0.4	11.0	<0.05	<0.05	----
3	Monroe St., below "	Carp	0.1	<0.4	11.0	<0.05	<0.05	----
4	Below State prison and Jackson	Carp	0.3	<0.4	8.0	<0.05	<0.05	----
5	State Street	Carp	0.3	<0.4	11.0	<0.05	<0.05	----
		Sucker	0.2	<0.4	8.0	<0.05	<0.05	----
6	Tompkins Road	Carp	0.3	<0.4	11.0	<0.05	<0.05	----
		Sucker	1.1	<0.4	12.0	0.5	<0.05	----
7	Columbia Road	Carp	0.2	<0.4	11.0	<0.05	<0.05	----
8	Creitz Road, above Lansing	Carp	0.1	<0.4	11.0	<0.05	<0.05	----
		Sucker	0.2	<0.4	8.0	<0.05	<0.05	----
		Bass	1.8	<0.4	8.0	0.5	<0.05	----
		Bullhead	1.8	<0.4	12.0	1.0	0.12	0.35
9	Above Red Cedar confluence	Carp	0.3	<0.4	11.0	<0.05	<0.05	----
10	Below Red Cedar confluence	Carp	0.1	<0.4	13.0	<0.05	<0.05	----
		Sucker	0.4	<0.4	9.0	<0.05	<0.05	0.2
11	Above Lansing WWTP	Carp	0.3	<0.4	12.0	<0.05	<0.05	----
12	Below Lansing WWTP	Carp	0.3	<0.4	8.0	<0.05	<0.05	----
13	State Road	Carp	0.4	<0.4	8.0	<0.05	<0.05	----
		Sucker	0.2	<0.4	12.0	<0.05	<0.05	----
14	Portland State Game Area	Carp	1.0	<0.4	13.0	<0.05	<0.05	----
		Sucker	0.0	<0.4	9.0	<0.05	<0.05	----
15	Lyons-Muir	Pike	0.2	<0.4	12.0	0.2	<0.05	0.45
21	Below Grandville, Wyoming, Grand Rapids	Carp	0.3	<0.4	12.0	<0.05	<0.05	----
		Sucker	0.0	<0.4	12.0	<0.05	<0.05	0.0
		Catfish	0.4	<0.4	12.0	<0.05	<0.05	0.45
22	Eastmanville	Carp	0.3	<0.4	8.0	<0.05	<0.05	----
		Sucker	0.0	<0.4	8.5	<0.05	<0.05	----
24	Grand Haven	Carp	0.6	<0.4	20.0	<0.05	<0.05	----
		Sucker	0.0	<0.4	23.0	<0.05	<0.05	----

Table 28. Concentrations of heavy metals in fish from Kalamazoo River, July, 1971. (Concentrations in ppm, wet weight).

Location	Species	Length	Hg	Cr	Ni	Pb	Zn	Cu	Cd	As
S1	White sucker	13.5	0.05	---	<0.5	<1.0	5.3	<0.1	<0.1	<0.5
	Rock bass	7.5	0.30	---	<0.5	<1.0	11.0	1.2	<0.1	<0.5
	Northern pike	17.0	0.33	---	<0.5	<1.0	6.7	0.1	<0.1	<0.5
S2	White sucker	15.5	0.30	<0.1	<0.2	<1.0	7.0	0.4	<0.1	<0.5
	Rock bass	7.0	0.13	<0.1	<0.2	<1.0	10.0	0.25	<0.1	<0.5
	Smallmouth bass	9.0	0.03	<0.1	<0.2	<1.0	7.0	0.2	<0.1	<0.5
	Bullhead	---	0.06	<0.1	<0.2	<1.0	16.0	0.2	<0.1	<0.5
N1	Carp	16.0	0.0	<0.1	<0.2	2.0	13.0	1.0	<0.1	<0.5
	Rock bass	6.0	0.05	<0.1	<0.2	1.0	10.0	0.3	<0.1	<0.5
	Bullhead	---	0.12	<0.1	<0.2	<1.0	10.0	0.3	<0.1	<0.5
N2	Carp	---	0.0	<0.1	<0.2	<1.0	6.0	0.3	<0.1	<0.5
	White sucker	---	0.05	<0.1	<0.2	<1.0	5.6	0.6	<0.1	<0.5
	Rock bass	---	0.08	<0.1	<0.2	<1.0	7.2	0.2	<0.1	<0.5
	Smallmouth bass	---	0.10	<0.1	<0.2	<1.0	5.6	0.2	<0.1	<0.5
	Bullhead	11.0	0.27	<0.1	<0.2	<1.0	6.4	0.3	<0.1	<0.5
	Northern pike	---	0.15	<0.1	<0.2	<1.0	7.2	0.1	<0.1	<0.5
M1	Carp	---	0.0	---	<0.5	<1.0	6.7	<0.1	<0.1	<0.5
	White sucker	---	0.13	<0.1	<0.2	<1.0	10.0	0.0	<0.1	<0.5
	Northern pike	---	0.20	<0.1	<0.2	<1.0	5.2	0.13	<0.1	<0.5
M2	Carp	---	0.0	<0.1	<0.2	<1.0	5.8	0.13	<0.1	<0.5
	White sucker	---	0.06	<0.1	<0.2	<1.0	9.0	0.20	<0.1	<0.5
	Rock bass	---	0.13	<0.1	<0.2	<1.0	10.0	0.20	<0.1	<0.5
	Northern pike	17.0	0.26	<0.1	<0.2	<1.0	7.5	0.13	<0.1	<0.5
M3	Carp	9.0	0.13	---	<0.5	<1.0	6.1	<0.1	<0.1	<0.5
	White sucker	8.0	0.07	---	<0.5	<1.0	6.7	0.3	<0.1	<0.5
	Rock bass	---	0.07	---	<0.5	<1.0	7.5	0.2	<0.1	<0.5
M4	Carp	---	0.0	---	<0.2	<1.0	8.0	0.3	<0.1	<0.5
	White sucker	---	0.12	---	<0.2	<1.0	5.0	0.3	<0.1	<0.5
	Northern pike	30.0	0.40	---	<0.2	<1.0	10.0	0.3	<0.1	<0.5
M5	Carp	---	0.13	---	<0.2	<1.0	10.0	1.3	<0.1	<0.5
	White sucker	---	0.13	---	<0.2	<1.0	15.0	0.3	<0.1	<0.5
	Rock bass	---	0.13	---	<0.2	<1.0	13.0	0.6	<0.1	<0.5
	Bullhead	---	0.06	---	<0.2	<1.0	8.0	0.4	<0.1	<0.5
M6	Carp	---	0.06	---	<0.2	<1.0	8.0	0.9	<0.1	<0.5
	White sucker	---	0.27	---	<0.2	<1.0	11.0	0.5	<0.1	<0.5
	Bullhead	---	0.06	---	<0.2	<1.0	13.0	0.4	<0.1	<0.5
M7	Carp	11.0	0.33	<0.1	<0.2	<1.0	20.0	0.5	<0.1	<0.5
	White sucker	---	0.06	<0.1	<0.2	<1.0	17.0	0.2	<0.1	<0.5
	Bullhead	---	0.15	<0.1	<0.2	<1.0	13.0	0.2	<0.1	<0.5
M8	Carp	---	0.06	---	<0.2	<1.0	9.0	0.0	<0.1	<0.5
	White sucker	---	0.13	<0.1	<0.2	<1.0	10.0	0.4	<0.1	<0.5
M9	Carp	---	0.20	<0.1	<0.2	<1.0	20.0	1.0	<0.1	<0.5
	White sucker	---	0.13	<0.1	<0.2	2.3	13.0	0.4	<0.1	<0.5
	Northern pike	---	0.10	---	<0.2	<1.0	25.0	0.5	<0.1	<0.5
M10	Carp	---	0.23	<0.1	<0.2	<1.0	15.0	0.2	<0.1	<0.5
	White sucker	9.0	0.00	<0.1	<0.2	<1.0	14.0	0.2	<0.1	<0.5
	Bullhead	6.3	0.50	<0.1	<0.2	<1.0	13.0	0.2	<0.1	<0.5
	Northern pike	14.0	0.37	<0.1	<0.2	<1.0	17.0	0.2	<0.1	<0.5
M11	Carp	---	0.20	<0.1	<0.2	<1.0	22.0	0.2	<0.1	<0.5
	White sucker	---	0.06	<0.1	<0.2	<1.0	9.0	1.2	<0.1	<0.5
	Bullhead	7.0	0.27	<0.1	<0.2	1.7	9.0	0.4	<0.1	<0.5
	Northern pike	17.5	0.05	<0.1	<0.2	<1.0	16.0	0.0	<0.1	<0.5

TABLE 29. HEAVY METAL CONCENTRATIONS IN FISH (EDIBLE PORTION) FROM TRIBUTARIES TO LAKE MICHIGAN, JUNE AND JULY 1971
(ANALYSIS BY MICHIGAN DEPARTMENT OF AGRICULTURE.)

	Metals in Parts Per Million Wet Weight													
BACKGROUND LOCATIONS	Hg	Cd	Pb	Cr	Ni	Cu	Zn	Mo	Co	Mn	Be	As	V	Se
Crockery Cr., Ellis Rd. Muskegon Co.														
Rock bass	0.4	0.2	0.1	N.D.	N.D.	0.7	14	0.1	0.2	0.5	0.02	---	N.D.	N.D.
Crockery Cr., I-96 Ottawa Co.														
Northern Pike	0.3	0.2	0.2	N.D.	N.D.	0.4	12	0.1	0.1	0.6	0.02	---	N.D.	N.D.
Flowers Fields Cr. Bowers Rd. St. Joseph Co.														
White suckers	0.1	N.D.	0.2	0.1	0.2	0.5	16	0.1	0.1	0.9	N.D.	0.027	N.D.	N.D.
Rock bass	0.4	0.1	0.2	0.2	0.3	0.5	26	N.D.	0.1	0.4	N.D.	0.036	N.D.	N.D.
Petoskey, Tannery Cr. Country Club Rd. Emmet Co.														
Brook trout	0.1	0.1	0.2	0.2	0.4	1.0	20	N.D.	0.1	0.3	N.D.	0.071	N.D.	N.D.
CONTAMINATED LOCATIONS														
Paw Paw R. below Watervliet Paper Co., Berrien Co.														
Carp	0.2	N.D.	0.1	0.3	0.4	0.7	22	N.D.	0.1	0.4	N.D.	0.120	N.D.	N.D.
Largemouth bass	0.4	0.1	0.1	0.3	0.2	0.4	9	N.D.	0.1	0.3	N.D.	0.240	N.D.	N.D.
Pigeon R. below White Pigeon Paper Mill, Berrien Co.														
Bowfin	0.4	N.D.	0.1	0.3	N.D.	0.4	6	N.D.	0.1	0.4	N.D.	0.120	N.D.	N.D.
Rock bass	0.5*	0.1	0.2	0.3	0.2	0.5	15	N.D.	0.1	1.0	N.D.	0.047	N.D.	N.D.
Portage Cr. below Allied Paper in Kalamazoo, Kalamazoo Co.														
Rock bass	0.7*	0.1	0.4	0.4	0.1	0.5	16	0.1	0.1	0.3	N.D.	0.055	N.D.	N.D.
Suckers	0.1	N.D.	0.3	0.2	0.1	0.6	12	N.D.	0.1	0.5	N.D.	0.037	N.D.	N.D.
Kalamazoo R. below Battle Creek WWTP, Calhoun Co.														
Carp	0.1	N.D.	0.2	0.3	0.1	0.5	28	N.D.	0.1	0.5	N.D.	0.049	N.D.	N.D.
Northern pike	0.1	0.1	0.1	0.2	0.2	0.4	13	0.1	0.1	0.6	N.D.	0.032	N.D.	N.D.
Crappie	0.1	0.1	0.1	0.2	0.2	0.4	17	0.1	0.2	1.0	N.D.	0.065	N.D.	N.D.
Grand R. below Jackson WWTP, Jackson Co.														
Suckers	0.2	0.1	0.1	0.3	N.D.	0.8	23	0.1	0.1	0.6	0.02	0.029	N.D.	N.D.
Carp	N.D.	0.2	0.8	0.5	N.D.	0.7	27	N.D.	0.2	0.5	N.D.	0.075	N.D.	N.D.
Grand R. between Grand Ledge & Lansing WWTP, Ingham Co. and Eaton Co.														
Carp	0.2	0.2	0.2	0.3	N.D.	0.8	45	0.1	0.2	0.6	0.02	0.051	N.D.	N.D.
Goldfish	0.3	0.2	0.9	0.4	N.D.	1.1	32	0.1	0.1	0.7	N.D.	0.057	N.D.	N.D.

TABLE 29 (CONTINUED)

(CONTAMINATED LOCATIONS CONTINUED)	Metals in Parts Per Million Wet Weight													
	Hg	Cd	Pb	Cr	Ni	Cu	Zn	Mo	Co	Mn	Be	As	V	Se
Grand R. offshore Grand Rapids Packaging Corp. of America, Kent Co.														
Carp	0.1	0.2	0.2	N.D.	N.D.	1.0	16	0.1	N.D.	0.3	N.D.	---	N.D.	N.D.
Redhorse	0.3	0.3	0.1	N.D.	N.D.	0.8	12	N.D.	0.2	0.6	0.02	---	N.D.	N.D.
White L. Muskegon Co., offshore Hooker Chemical Co.														
Northern pike	0.8*	0.1	1.3	0.3	N.D.	0.8	16	N.D.	0.2	0.6	N.D.	0.400	N.D.	N.D.
Rock bass	0.6*	0.1	0.3	0.4	N.D.	0.3	14	N.D.	0.2	0.4	N.D.	0.083	N.D.	N.D.
Yellow perch	0.4	0.1	0.1	0.2	---	1.0	22	N.D.	0.2	0.8	N.D.	---	N.D.	N.D.
Grand Rapids below WWTP Kent Co.														
Red horse suckers	0.1	0.1	0.1	0.2	0.2	0.6	10	0.1	0.2	0.8	0.02	---	N.D.	N.D.
Carp	0.1	0.2	0.3	0.3	0.2	4.4	37	N.D.	0.1	0.8	N.D.	---	N.D.	N.D.
Menominee R. offshore Ansul Chem. Co., Menominee Co.														
Walleye	0.4	0.1	0.1	0.4	0.3	0.7	9	N.D.	0.1	0.3	N.D.	0.210	N.D.	N.D.
Smallmouth bass	1.3*	0.2	0.1	0.4	0.4	---	---	N.D.	0.2	0.5	N.D.	0.150	N.D.	N.D.
White L. offshore Muskegon Leather Tannery														
Northern pike	0.4	0.1	0.2	0.2	0.1	0.4	22	N.D.	0.2	0.3	N.D.	0.245	N.D.	N.D.
Yellow perch	0.3	0.1	0.1	0.2	0.1	0.3	15	N.D.	0.2	0.5	N.D.	0.021	N.D.	N.D.
Rock bass	0.4	0.1	0.1	0.3	0.4	0.4	19	N.D.	0.3	0.4	N.D.	0.073	N.D.	N.D.
Little Black Cr. below Muskegon Heights WWTP Muskegon Co.														
Carp	0.1	N.D.	0.2	0.4	0.2	0.5	24	N.D.	0.1	0.4	N.D.	0.098	N.D.	N.D.
Lake Macatawa, Pine Cr. Bay Holland, Ottawa Co.														
Northern pike	0.2	0.1	0.2	0.2	0.3	0.3	16	N.D.	0.1	0.3	N.D.	0.255	N.D.	N.D.
Channel catfish	0.3	0.1	0.1	0.2	0.4	0.3	16	N.D.	0.2	0.3	N.D.	0.190	N.D.	N.D.
Grand Haven Grand R. south channel, Ottawa Co.														
Carp	0.8*	0.1	0.2	0.2	0.4	0.5	25	N.D.	0.1	0.4	N.D.	0.230	N.D.	N.D.
Mona L. mouth of Little Black Cr., Muskegon Co.														
Carp	0.2	0.1	0.3	0.2	0.2	0.6	23	N.D.	0.1	0.5	N.D.	0.031	N.D.	N.D.
Channel catfish	0.1	N.D.	0.2	0.1	0.2	0.2	17	N.D.	0.1	0.2	N.D.	0.110	N.D.	N.D.
Sucker	0.1	N.D.	0.2	0.2	0.2	0.4	13	N.D.	0.1	0.5	N.D.	0.022	N.D.	N.D.
Rogue R. below Rockford Paper Mill, Kent Co.														
Burbot	0.2	0.1	0.3	0.1	0.2	0.5	15	0.1	0.1	0.6	N.D.	0.190	N.D.	N.D.
Rainbow trout	0.1	0.1	0.3	0.1	0.5	0.5	14	N.D.	0.2	0.7	N.D.	0.036	N.D.	N.D.
Northern pike	0.2	N.D.	0.2	0.1	0.2	0.3	16	0.1	0.1	0.7	N.D.	0.052	N.D.	N.D.
Minimum	N.D.	N.D.	0.1	N.D.	N.D.	0.2	6	N.D.	N.D.	0.2	N.D.	0.021	N.D.	N.D.
Maximum	1.3	0.3	1.3	0.4	0.5	4.4	45	0.1	0.3	1.0	0.02	0.400	N.D.	N.D.
Mean	0.3	0.1	0.2	0.2	0.2	0.7	19	0.03	0.1	0.5	0.003	0.106	N.D.	N.D.

* Concentration exceeds FDA interim guideline

TABLE 30. PHS STANDARDS FOR RAW WATER SUPPLIES

Element	Concentration (mg/l)
Arsenic (As)	0.05
Barium (Ba)	1.0
Cadmium (Cd)	0.01
Chromium, hexavalent (Cr^{+6})	0.2
Copper (Cu)	1.0
Iron (Fe)	0.3
Manganese (Mn)	0.05
Selenium (Se)	0.01
Silver (Ag)	0.05
Zinc (Zn)	5.0

TABLE 31. TOXICITY OF METALS TO AQUATIC ORGANISMS

Toxicant	Organism	Reference	Test Duration	Effect Observed	Water Hardness (mg/l as C_aCO_3)	Concentration (mg/l) Effect	No Effect
Aluminum	Rainbow trout	Freeman & Everhart 1971	8 weeks	Mortality & growth	25	0.52	0.05
	Daphnids	*Biesinger & Christensen, unpublished data	3 weeks	Reproduction	45	0.68	0.32
Arsenic	Daphnids	"	3 weeks	Reproduction	45	1.40	0.52
Barium	Daphnids	"	3 weeks	Reproduction	45	8.90	5.80
Cadmium	Bluegill	*Eaton, unpublished	10 months	Adult Mortality fry survival	200	0.111	0.037
	Brook trout	*Eaton & McKim, unpublished	30 days	Egg & fry survival	45	0.111	0.004
	Lake trout	"	30 days	Egg & fry survival	45	0.011	0.004
	Coho salmon	"	30 days	Egg & fry survival	45	0.004	0.001
	Brown trout	"	30 days	Egg & fry survival	45	0.011	0.004
	Steelhead	*Chapman, unpublished	96 hrs.	Mortality	20	0.003	-----
	Coho	"	7 days	Fry survival or mortality	20	0.0019	0.0011
	Chinook	"	7 days	Fry mortality	20	0.0006	------

* This data is preliminary and unpublished and should not be used without the researcher's consent.

TABLE 31 (CONTINUED)

Toxicant	Organism	Reference	Test Duration	Effect Observed	Water Hardness (mg/l as C_aCO_3)	Concentration (mg/l) Effect	No Effect
Cadmium	Coho	*Chapman, unpublished	96 hrs.	Fry Mortality	20	0.002	0.0005
	Chinook (static)	"	7 days	Fry Mortality	20	0.001	0.0006
	Daphnids	*Biesinger & Christensen	3 weeks	Reproduction	45	0.0007	0.0002
	Rainbow trout	Ball, 1967 (b)	7 days	TLm**	290	0.01	------
	Fathead minnows	*Pickering & Gast 1971	10 months	Reproduction	200	.057	.037
Chromium^{+6}	Fathead minnows	*Pickering, unpublished	96 hrs.	TLm	200	33.0	------
	Fathead minnows	"	10 months	Reproduction	200	2.0	1.0
	Brook trout	*Benoit, unpublished	2 years	Reproduction	45	0.40	0.20
	Brook trout	"	96 hrs.	TLm	45	50.0	------
	Rainbow trout	"	2 years	Reproduction	45	0.40	0.20
	Rainbow trout	"	96 hrs.	TLm	45	69.0	------
	Largemouth bass	Fromm & Schiffman 1958	48 hrs.	TLm	334	195	------
	Largemouth bass	"	80 hrs.	TLm	334	94	------
	Fatheads	Pickering & Henderson, 1964	96 hrs.	TLm	20	17.6	------
	Bluegills	"	96 hrs.	TLm	20	118	------
	Fatheads	"	96 hrs.	TLm	360	27.3	------
	Bluegills	"	96 hrs.	TLm	360	133	------
Cr^{+3}	Fatheads	Pickering & Henderson, 1964	96 hrs.	TLm	20	5.07	------
	Bluegills	"	96 hrs.	TLm	20	7.46	------

* This data is preliminary and unpublished and should not be used without the researcher's consent.

** TLm = median tolerance limit; the concentration of a toxicant which results in a 50% mortality of test organisms in the specified exposure time.

TABLE 31 (CONTINUED)

Toxicant	Organism	Reference	Test Duration	Effect Observed	Water Hardness (mg/l as C_aCO_3)	Concentration (mg/l) Effect	No Effect
Cr^{+3}	Fatheads	Pickering & Henderson, 1964	96 hrs.	TLm	360	67.4	------
	Bluegills	"	96 hrs.	TLm	360	71.9	------
	Daphnids	*Biesinger & Christensen	3 weeks	Reproduction	45	0.600	0.330
	Hexagenia nymphs	1970 Winona State College	96 hrs.	Mortality	357-448	8.6	------
Copper	Rainbow trout	*McKim & Eaton, unpublished	30 days	Egg & fry survival	45	0.037	0.012
	Lake herring	"	30 days	Egg & fry survival	45	0.111	0.037
	Brook trout	"	30 days	Egg & fry survival	45	0.037	0.019
	Lake trout	"	30 days	Egg & fry survival	45	0.111	0.037
	Brown trout	"	30 days	Egg & fry survival	45	0.037	0.019
	Daphnids	*Biesinger & Christensen, unpub.	3 weeks	Reproduction	45	0.035	0.022
	Coho	*Chapman, unpublished	96 hrs.	Fry mortality	20	0.045	0.030
	Chinook	"	96 hrs.	Fry mortality	20	0.100	0.030
	Steelhead	"	96 hrs.	Fry mortality	20	0.030	0.015
	White sucker	*McKim & Eaton, unpublished	30 days	Egg & fry survival	45	0.037	0.012
	Bluegill	*Benoit, unpublished	2 years	Reproduction	45	0.080	0.040
	Bluegill	"	96 hrs.	TLm	45	1.10	------
	Campeloma	Arthur & Leonard 1971	Chronic	Reduction in survival of adults	45	0.0148	0.008
	Physa	"			45	0.0148	0.008
	Gammarus		Chronic	Reduction in survival of adults	45	0.008	0.005
	Fathead minnow	Mount, 1968	Life cycle	Growth	198	0.095	0.015
			11 months	Spawning	198	0.032	------
			96 hrs.	TLm	198	0.430	------
	King salmon (sacfry)	Hazel & Meith, 1970	Sacfry to swim up stage	% Survival to swim up stage reduced to 5.6% survival of sac fry reduced to 6.85%	44	0.040	------

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TABLE 31 (CONTINUED)

Toxicant	Organism	Reference	Test Duration	Effect Observed	Water Hardness (mg/l as C_aCO_3)	Concentration (mg/l) Effect	No Effect
Copper							
	Sockeye & pink salmon	Martens, Gordon, Servizi; 1970	Egg to fry (yolk absorption)	Mortality and (retarded) development		0.025	------
	Brook trout	McKim & Benoit, 1971	11 month	Mortality, growth	45	0.0175	0.0095
			96 hrs.	TLm	45	0.10	
	Crayfish, Orconectes rusticus	Hubschman 1967		Reproduction	100-125	0.125	0.06
	Rainbow trout	Brown & Dalton, 1970	48 hrs.	Mortality	240	0.75	------
	Fatheads	Mount & Stephan, 1969	10 months	Survival, growth and reproduction	31.4	0.018	0.011
	Fathead minnow	"	96 hrs.	TLm	31.4	0.075	------
	Ephemerella subvaria	Winona St. College, 1970	48 hrs.	TLm		0.32	------
	Acroneuria Tycerias	"	96 hrs.	TLm		8.3	------
	Hexagenia bilineata	"	48 hrs.	TLm		0.22	------
Iron	Daphnids	*Biesinger & Christensen, unpub.	3 weeks	Reproduction	34	5.20	4.38
	Brook trout	*Sykora	37 weeks	Growth	120	12.0	6.0
	Fathead minnow	"	5 months	Mortality	120	50.0	25.0
	Gammarids	"	4 months	Reproduction	120	3.0	1.5
	Caddisflies	"	2 months	Emergence	120	25.0	12.0
Lead	Daphnids	*Biesinger & Christensen, unpub.	3 weeks	Reproduction	45	0.100	0.030

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TABLE 31 (CONTINUED)

Toxicant	Organism	Reference	Test Duration	Effect Observed	Water Hardness (mg/l as C_aCO_3)	Concentration (mg/l) Effect	No Effect
Lead	Coho	*Chapman, unpublished	96 hrs.	Fry mortality	20	0.300	0.100
	Chinook	"	96 hrs.	Fry mortality	20	1.000	0.600
	Steelhead	"	96 hrs.	Fry mortality	20	0.600	0.300
	Brook trout	*McKim, unpublished	3 weeks	Fry mortality	45	0.500	0.250
	Rainbow trout	*Everhart, unpublished	18 days	Sub-adult mortality	27	0.140	------
			19 months	Deformity	27	0.012	------
	Rainbow trout	"	4 days	Sub-adult mortality	335	0.140	------
			19 months	Deformity	335	0.018	------
	Fatheads	Pickering & Henderson, 1964	96 hrs.	TLm	20	5.58	------
	Bluegills	"	96 hrs.	TLm	20	23.8	------
Magnesium	Daphnids	*Biesinger & Christensen, unpub.	3 weeks	Reproduction	45	82.0	125.0
Manganese	Daphnids	"	3 weeks	Reproduction	45	5.20	4.10
Nickel	Daphnids	"	3 weeks	Reproduction	45	0.095	0.030
	Fathead minnows	*Pickering, unpublished manuscript	96 hrs.	TLm	200	27.0	------
	Fathead	"	11 months	Reproduction	200	0.73	0.38
	Rainbow trout	Brown & Dalton, 1970	48 hrs.	TLm	240	32.0	------
	Fatheads	Pickering & Henderson 1964	96 hrs.	TLm	20	4.58	------
	Bluegills	"	96 hrs.	TLm	20	5.18	------
	Fatheads	"	96 hrs.	TLm	360	43	------
	Bluegills	"	96 hrs.	TLm	360	40	------
	Hexagenia bilineata	Winona State College, 1970	96 hrs.	Mortality		No mortality 27.2	
	Rainbow trout	Willford, 1967	48 hrs.	TLm		160	

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TABLE 31 (CONTINUED)

Toxicant	Organism	Reference	Test Duration	Effect Observed	Water Hardness (mg/l as C_aCO_3)	Concentration (mg/l) Effect	No Effect
	Lake trout	Willford, 1967	48 hrs.	TLm		75	------
	Brook trout	"	48 hrs.	TLm		242	------
Zinc	Daphnids	*Biesinger & Christensen, unpub.	3 weeks	Reproduction	45	0.102	0.070
	Coho	*Chapman, unpublished	96 hrs.	Fry mortality	20	0.140	0.100
	Chinook	"	96 hrs.	Fry mortality	20	0.600	------
	Chinook	"	96 hrs.	Fry mortality	20	0.300	0.250
	Steelhead	"	96 hrs.	Fry mortality	20	0.300	0.100
	Bluegills	Cairns & Scheier, 1968	96 hrs.	TLm	45	2.86	------
	Rainbow trout	Ball, 1967 (a)	5 days	TLm	290	4.60	------
	Fathead	Brungs, 1969	10 months	Reproduction	200	0.18	0.03
	Fathead	"	96 hrs.	TLm	200	9.2	------
	Fathead	Mount, 1966	96 hrs.	TLm	50(pH:8)	4.9	------
				TLm	100(pH:8)	9.0	------
				TLm	200(pH:8)	11.9	------
				TLm	240	4.0	------
	Rainbow trout	Brown & Dalton, 1970	48 hrs.	TLm	20	.87	------
	Fathead minnows	Pickering & Henderson, 1964	96 hrs.	TLm	360	33.4	------
	Bluegills	"	96 hrs.	TLm	20	5.38	------
			96 hrs.	TLm	360	40.9	------
	Atlantic salmon fingerlings; yolk sac fry of salmon, brown trout and rainbow trout	Grande, 1966	21 days	Mortality			0.5-1.0
	Rainbow trout	Sprague, 1968		Avoidance	13-15	.006	

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